SERVICE CHEMISTRY

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SERVICE CHEMISTRY.

SERVICE CHEMISTRY:

BEING

A Short Manual of Chemistry

From
W. B. WHITTINGHAM & CO.,
91, GRACECHURCH STREET, LONDON.

With the Publishers' Compliments.

Professor of Chemistry, Royal Naval College, Greenwich; Associate of the Institution of Naval Architects, &c., &c.

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No.

PREFACE.

IN the absence of any text-book dealing with the Chemical treatment of subjects of such paramount importance to the Services as Explosives, Fuel, Drinking Waters, Boiler Incrustation, Corrosion and Fouling of Ships, Paints, Ventilation, &c., it became necessary to prepare one for the Officers passing through the Royal Naval College; and in doing so, I have endeavoured to develop in a rational way the main facts of the Science, and the theories which are deduced from them, and have then amplified those portions which touch on Service questions as fully as possible; whilst those parts of the subject which are likely to be of less immediate importance to the readers for whom the book is intended, are condensed as far as is advisable.

Whilst using the title "Service Chemistry," I wish it to be clearly understood that there is but one Chemistry, and that its technical adaptation to any special subject is merely an amplification of the Science in a particular direction, which cannot be properly done without at the same time mastering the general principles of which the technical application merely forms a small branch, and that a knowledge of the chief principles and theories of Chemistry is absolutely essential before any useful application of the Science is possible.

The limited time at the disposal of the Officers of both branches of the Service, over and above that required for purely professional work, renders it impossible for them to undertake any such extended course of general study as would justify the subsequent employment of technicalities without full explanation; and I have, therefore, as far as the limits of the book will allow, gone fully into details of manufacture and other subjects generally considered beyond the scope of a chemical manual, as, for instance, in the chapter on Gunpowder, where the manufacture, proving and keeping of powders are treated as fully as the chemistry of its composition and explosion.

In the special portions of the book a large proportion of the matter is original whilst in the general part some new forms of experiments will be found.

I wish to acknowledge the valuable aid of Major Barker in many matters connected with Explosives, and also the help afforded me by the published researches of Dr. Debus and Sir Frederick Abel, and Major-General Wardell's admirable book on Gunpowder and Guncotton (from which the illustration of the hydraulic prism press, by the late J. F. Wardell, has been copied).

Much care has been bestowed on the Index, which will, I hope, be found fairly complete, and in conclusion I desire to express my indebtedness to my colleague, Mr. W. Popplewell Bloxam, B.Sc., for the great aid he has given me in his careful revision and correction of the proofs, and also to Mr. W. J. Orsman for his general help.

V. B. L.

ROYAL NAVAL COLLEGE, GREENWICH,
October, 1889

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ERRATA.

Page 13, *line* 18, instead of "all gases," read "all gases with the exception of hydrogen."

,, 59, ,, 12, read "Fig. 19" instead of "Fig. 16."

,, 66, ,, 28, omit the words "to proceed."

,, 131, ,, 17, insert the sign "+" in second part of equation.

,, 139, ,, 19, read "Napthalene" instead of "Napthaline."

,, 143, ,, 15, read "(B, Fig. 31)" instead of "(B, Fig. 29)."

,, 343, *last line*, read "$4(H_2O)$" instead of "H_2O."

,, 412, *line* 16, place "is" at commencement instead of end of line.

,, 414, ,, 25, read "the metal silver" instead of "silver metal."

SERVICE CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

Physical and chemical change—Conservation of matter and energy—Elements—Mechanical mixtures and chemical compounds—Laws of combination—Molecules and atoms—States of aggregation—Symbols—Formulæ and Equations—Atomic and molecular weight—Effect of temperature and pressure on gases—Law of Avogadro—Nomenclature.

CAREFUL observation shows us that two great methods of change are always at work altering the face of Nature and the forms of matter which are found on the globe.

We see granite rocks being gradually broken down by the combined action of water and frost, yet the fragments torn from the rock are of the same composition as the rock itself. We know that by cold we can convert water into ice, and by heat into steam; yet the solid ice—the liquid water—and the gaseous steam have all the same composition. We see a coil of platinum wire heated to a temperature at which it acquires the power of giving out light; yet on cooling, the platinum once more loses this property and is found to be in no way changed from the original metal, being chemically identical and no change in weight having taken place. Changes of this kind, in which form and properties only undergo modification, without any alteration in composition, are called Physical changes, and the study of this class of phenomena comes under the domain of Physical Science.

A second kind of change, however, is at work, in which the alteration affects not only the physical properties of the original mass, but also its composition. A fallen tree, exposed to air and moisture, gradually rots away and is converted into gases and soil. A candle burns, and the wax of which it is composed disappears. A metal dissolved in an acid loses its metallic properties and remains in solution in the liquid. A piece of magnesium wire, heated in contact with air, emits light, burns away, and at the end of the operation we have a white powder left which is entirely different in form and properties from the metal magnesium. In all these cases a change of weight, as well as of properties and composition, has taken place; and if we collected and weighed the white powder formed during the combustion of the magnesium wire, it would be found to weigh more than the metal burnt. Changes of this class, in composition as well as properties, are called Chemical changes, and the study of the laws which

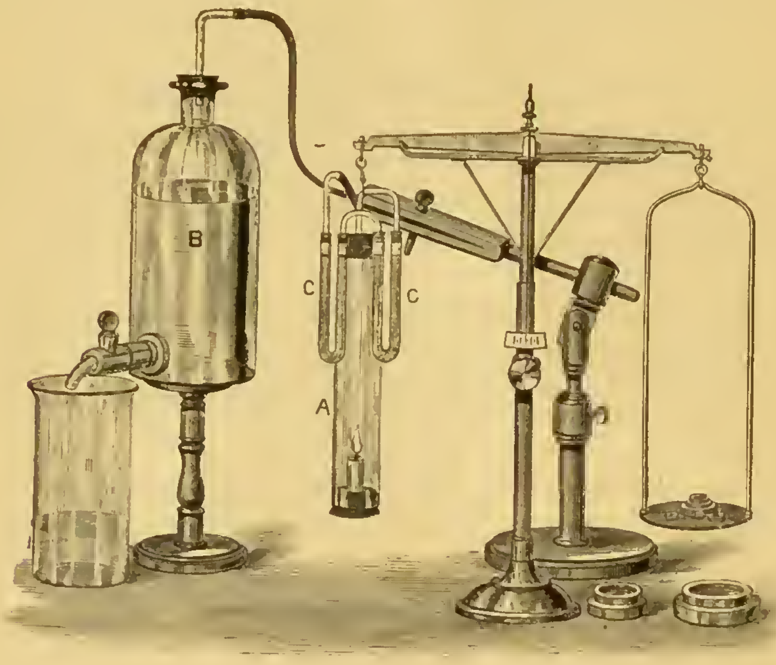

Fig. 1.

govern and bring about such changes constitute the *Science of Chemistry.*

In Nature no such thing as loss or creation of matter occurs, although in many cases the products of the chemical changes taking place, being gaseous, escape our notice, as when a candle burns.

If, instead of allowing the candle to burn in the open air, it had been supported in a glass cylinder (A, Fig. 1) and the products of its combustion had been drawn by means of the aspirator bottle (B) through tubes (C) (C), containing small fragments of sodic hydrate, which has the power of absorbing carbon dioxide and water vapour (the gaseous compounds formed by the combustion of the wax of the candle), it could be shown that the products formed weighed more than the wax consumed, by suspending the candle and absorption tubes to one end of a balance, when, instead of losing weight, as might have been expected, from the diminution in size of the candle, the candle and

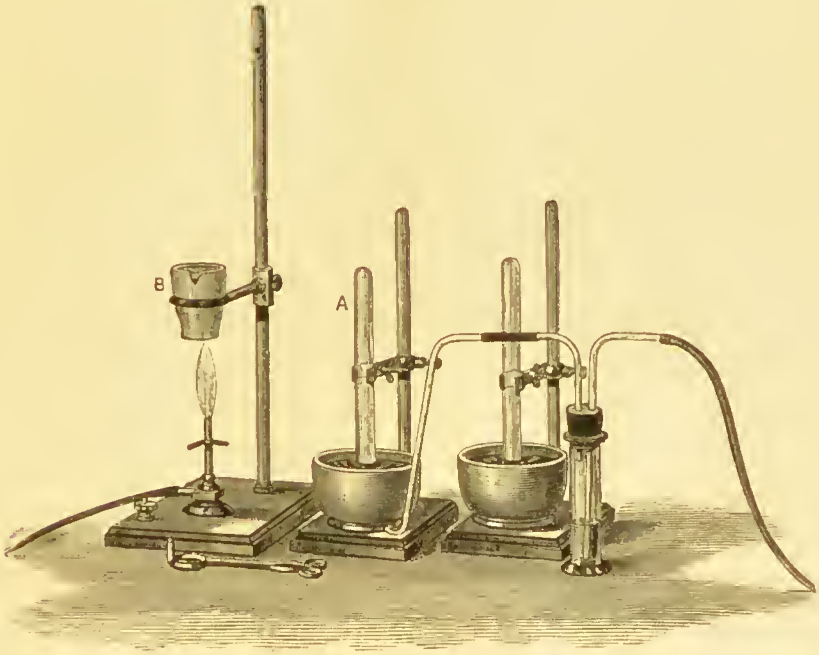

Fig. 2.

absorption tubes are seen to increase in weight, and this increment is due to the constituents of the wax having entered into chemical combination with one of the constituents of the air, the increase in weight shown by the balance being exactly equal to the loss of weight of the air.

If one of the constituents of the air, called oxygen, be allowed to pass, bubble by bubble, into a tube filled with mercury (A, Fig. 2), the mercury is displaced and the tube fills with the gas, but if it be bubbled up into a second in which a piece of well dried phosphorus has been passed to the top of the tube, and there melted by holding over it an inverted red-hot fire-clay crucible (B), each bubble of gas as it enters will cause a flash of light and no displacement of the mercury will take place until all action ceases: that is, until all the phosphorus has been converted into a compound of phosphorus and oxygen, called phosphoric pentoxide, which is left as a solid above the mercury in the tube. This oxide of phosphorus will be found to weigh exactly as much as the oxygen and phosphorus used up in its formation, and the apparent disappearance of the oxygen is merely due to the change on combination from the gaseous state to the solid. These facts are embodied in the general principle known as "The Conservation of Mass," which may be stated as follows—"The mass of matter which takes part in any change, whether physical or chemical, remains unaltered."

Chemical change may be brought about by several causes, one of the most powerful being heat; but, besides this, mechanical force will often set up chemical action, as when a percussion cap is struck; light, as in processes of photography; galvanic electricity, as when metals are deposited from solutions of their salts by means of a galvanic current; all these being forms of energy which aid or oppose chemical affinity, a force which acts at infinitely small distances, and which in only a few cases causes combination to take place between solids; the liquid or gaseous condition allowing closer contact between the particles of the re-acting bodies.

No chemical change can occur without being accompanied by some physical change, change of temperature being the most usual manifestation.

When chemical combination takes place, heat is generally evolved, and the amount of heat so given out is taken as a measure of the combining energy of the original substances. When such a compound is once more decomposed, heat is again absorbed and remains as latent chemical energy until combination once more takes place. For instance, when the two gases, oxygen and hydrogen, combine, great heat is evolved and water is formed, and in order to once more decompose this water the same quantity of heat or its equivalent in other forms of energy, is required. Energy, like matter, can be converted from one form into another, but cannot be created or destroyed, a principle known as the "Conservation of Energy."

If we take a small globule of mercury and warm it gently with strong nitric acid, the mercury dissolves with evolution of a gas which turns reddish-brown in air, and on carefully evaporating the solution, we can crystallise out a colourless salt called mercuric nitrate; on drying these crystals and again heating them, a reddish-brown gas is given off, and a red powder called mercuric oxide is left. This red powder, when placed in a hard glass tube and heated, breaks up into vapour of the metal mercury, which condenses in globules in the cool portion of the tube, whilst a colourless gas called oxygen is evolved, and can be conducted by the leading tube (B) under the surface of water in the pneumatic trough (C) and collected by displacement of water in the cylinder (D). (Fig. 3).

The question now naturally arises: can we go on decomposing substances in this way to an unlimited extent; further experiment shows us that we cannot. If we take mercury and oxygen and experiment on them, we find that they can be made to combine with other elements to form a large number of compounds, but by no means at present at our disposal can we sub-divide them into anything but mercury and oxygen.

When, in this way, a substance resists further decomposition, we call it an Element, and at present about sixty-seven such substances are known, and of these, as far as we know, all matter is built up. It is by no means unlikely that on the discovery of some new form of energy or method of analysis, we may be able to break up some of these into simpler bodies, and we therefore define an element as "a substance which by no means at present at our disposal can be decomposed into anything simpler."

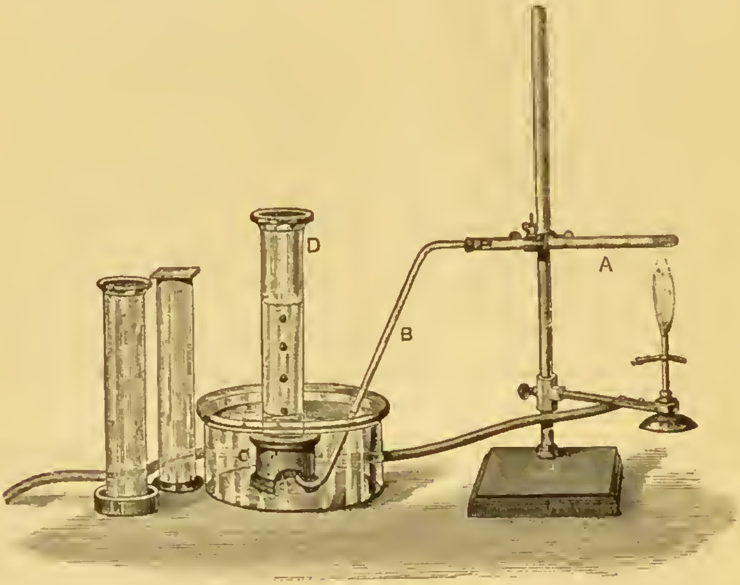

Fig. 3.

A list of the elements will be found at the end of this chapter (p. 25).

The distribution of the elements in Nature is most irregular. Some are found in very large quantities and very widely distributed; whilst others occur in such minute quantities that their properties are scarcely yet known. Indeed, nearly half the elements known at present might be eliminated without, as far as our present knowledge goes, causing any considerable disturbance of the laws of Nature.

The general distribution of the elements is roughly indicated in the following tables.

COMPOSITION OF AIR.

Nitrogen	76.9	parts by weight.
Oxygen	23.1	,, ,,
	100.0	

COMPOSITION OF WATER.

Oxygen	$88.\dot{8}$	parts by weight.
Hydrogen	$11.\dot{1}$	,, ,,
	$99.\dot{9}$	

APPROXIMATE COMPOSITION OF THE CRUST OF THE EARTH.

Oxygen	45.5
Silicon	29.4
Aluminium	8.2
Iron	6.3
Calcium	2.4
Magnesium	1.6
Sodium	2.5
Potassium	2.0
All the other elements	2.1
	100.0

To these elements must be added carbon, which exists in all matter of organic origin, and it is then seen that 99 per cent. of known substances are composed of eleven elements, whilst oxygen alone constitutes upwards of 52 per cent. of earth, air, and water.

Elements combine to form chemical compounds, or, more rarely, exist free.

When in mechanical mixture, the distinctive properties of the substances present are retained, although often modified by the properties of the other constituents; but in a chemical compound the properties of the original factors entirely disappear, and are merged in new characteristics distinctive of the compound formed.

Air is a mechanical mixture, and in air we recognise the properties of the great supporter of life and combustion—oxygen—modified and restrained by the distinctive properties of the other constituent, the inert nitrogen.

Water, on the other hand, is a chemical compound of oxygen and hydrogen, in which all the properties, chemical and physical, of the constituents have disappeared, and have given place to the distinctive characteristics of water.

If iron filings and finely powdered sulphur be mixed together, a greenish-grey powder is formed, in which, by means of a microscope, the particles of sulphur and iron may be seen lying side by side, and from which the iron and sulphur may be recovered by mechanical means, such as acting upon it by a magnet, which attracts and withdraws the iron, or by throwing it upon water, when the iron sinks. Such a powder is called a mechanical mixture, and has all the properties of the substances composing it.

If some of this mixture be heated a chemical action takes place, and the result is a black homogeneous mass in which no particles of sulphur or iron can be detected by the most powerful microscope: it is not magnetic, and when thrown on water it sinks as a whole, and the iron and sulphur can only be again obtained from it by complicated chemical processes.

The chemical compound so formed has none of the properties of the sulphur or the iron, but has acquired a new set of properties peculiar to itself.

If we take water and, having converted it into steam, pass it over iron heated to dull redness, we find that it is broken up into its constituents, the oxygen remaining combined with the iron, whilst hydrogen comes off free and may be collected by suitable arrangements. Iron is not the only metal which will do this; indeed, certain metals like sodium and potassium, will decompose water at ordinary temperatures, whilst magnesium only requires a temperature of 100° C. to effect the decomposition. The fact that we can obtain hydrogen gas from steam proves that hydrogen is one of the constituents of water; and we also find that if a mixture of steam and chlorine be passed through a heated porcelain tube, the steam is decomposed, the hydrogen and chlorine uniting to form hydrochloric acid whilst oxygen is liberated.

This is best done by generating chlorine gas by gently warming a mixture of hydrochloric acid and black oxide of manganese in the flask (A, Fig. 4), and leading the liberated chlorine through water in the retort (B) which is kept just at the boiling point by a water bath; the chlorine so saturated with water vapour is then passed through a porcelain tube heated to dull redness in the gas furnace (C)—a larger heating surface being obtained by filling the tube with pieces of broken porcelain or glass—under the influence of heat chlorine decomposes water vapour and the resulting oxygen and hydrochloric acid, together with any chlorine or steam which may have been in excess pass on, and if they are led into water in the pneumatic trough and collected by displacement of water in the cylinder (D), the chlorine and hydrochloric acid being soluble, will be absorbed by the water, any steam will be condensed, and nothing but oxygen will remain.

Pure water can be entirely converted into steam, and from the steam nothing but oxygen and hydrogen can be obtained; also if oxygen and hydrogen gases be mixed together in a strong open glass vessel and a flame be applied to the mouth, an explosion ensues with formation of water vapour, and we therefore say that water is a compound of the two gases, oxygen and hydrogen.

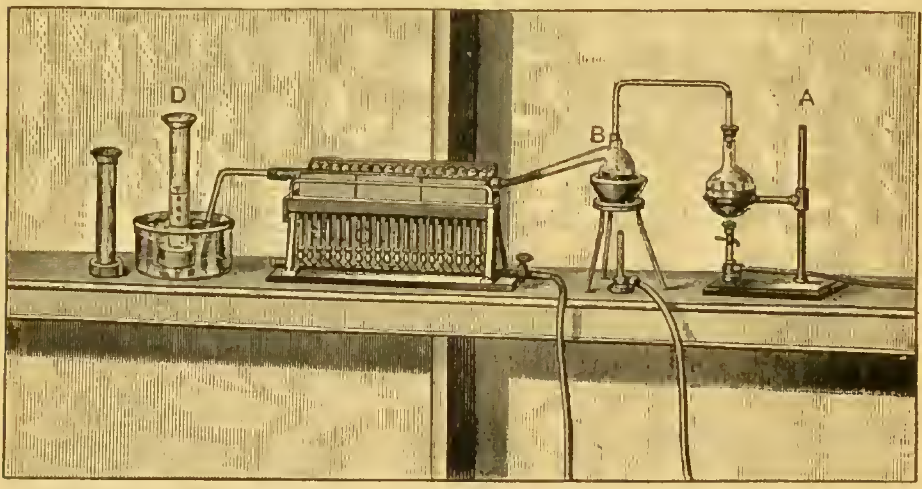

Fig. 4.

By passing a galvanic current through water acidulated with a few drops of sulphuric acid the water can be decomposed, the oxygen being liberated at the pole at which the current enters the liquid, and the hydrogen at the pole at which it leaves, and by using an apparatus of the kind shown in Fig. 5, the gases can be collected separately; and we always find that from a given weight of water we can obtain twice as much hydrogen by volume as oxygen; and, moreover, that *from a constant weight of water we always obtain these two gases in the same proportion by weight and by volume.*

The analysis of all the compounds with which we come in contact shows us that the formation of these compounds, and the proportions in which their constituents are combined follow certain definite laws :

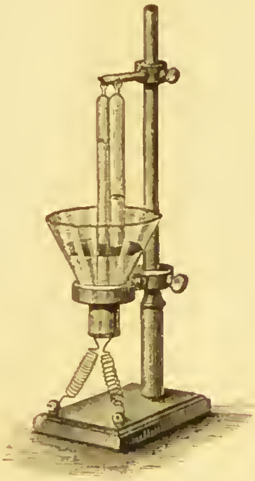

Fig. 5.

1. That every definite chemical compound has a fixed and invariable composition : that is, a given compound always consists of the same elements united in the same proportions. (Law of Constant Proportions.)

2. If one substance combines with another in more than one proportion, the several proportions are always some multiple of the lowest of these proportions. (Law of Multiple Proportions.)

This may be seen in the oxides of carbon.

Carbon monoxide contains 12 parts by weight of C to 16 parts of O.

Carbon dioxide contains 12 parts by weight of C to 32 parts of O; or for the same twelve parts by weight of C you have 16 or 16 × 2 parts by weight of oxygen.

A still more striking example of the law is seen in the oxides of nitrogen, in which 28 parts by weight of nitrogen combine with 16, 16 × 2, 16 × 3, 16 × 4, and 16 × 5 parts by weight of oxygen.

3. If the proportions by weight in which a series of bodies (B C D) combine with another body (A) be determined, these weights, or some multiple or sub-multiple thereof, are also the weights with which B C and D will combine amongst themselves. (Law of Reciprocal Proportion.)

One part by weight of H unites with 35.5 parts by weight of Cl, 35.5 × 2 parts by weight of Cl unite with 32 of sulphur, and 32 of sulphur unite with 1 × 2 of hydrogen.

When we heat a piece of sulphur, we find that at a temperature of 115° C. it melts to a limpid yellow liquid, which on further heating thickens, darkens, and at last volatilises and becomes a gas, the gas occupying many hundred times the volume of the sulphur taken.

In the same way, when water is boiled it is converted into steam, the vapour so formed occupying between 1,700 and 1,800 times the volume of the water taken. Roughly, a cubic inch of water forms a cubic foot of steam. This enormous increase of volume may be explained in one of two ways—either the cubic inch of water is stretched under the influence of heat, like a piece of india-rubber, until it assumes the dimensions of the cubic foot, or else the cubic inch of water is built up of an innumerable host of small particles, which when heated tend to repel each other and so cause the increase in volume.[*]

If the first theory be correct, then every part of the cubic foot of steam would be perfectly homogeneous, and without condensing some of the steam it would be impossible for any other vapour to find room in the space so occupied, whilst experiment shows us that one vapour acts as a vacuum to another,[†] so that other vapours can occupy the space already filled with water vapour; a phenomenon which can only be explained on the assumption that the vapours do not completely fill the space they occupy, although equally distributed through it; that is, they are built up of particles, which by the action of heat become widely separated from each other, thus leaving spaces within which the particles of other vapours may find place.

The states of aggregation of elementary bodies are, as far as we can ascertain, merely dependent upon temperature, all gases having been condensed by either cold, pressure, or a combination of the two, to the liquid state, whilst nearly all have been solidified.

If the vapours and gases consist of particles, then we must assume that liquids and solids also are built up in the same way, an assumption entirely borne out by experiment.

In the solid state, these particles, each of which has the same properties as the mass of which it is a part, are held together by the force of "cohesion," a force which varies with the nature of the substance; so that when a solid is heated, the particles tend to separate, but in different substances they do so to a different extent; as the stronger the force of cohesion existing between the particles, the greater is the work the heat has to do in separating them; at a certain temperature the particles are so far asunder that the force of cohesion is loosened to a certain extent and the particles become free to move around each other, *i.e.*, they assume the liquid state; continue the heating, the distances between the particles grow greater and greater until a point is reached at which cohesion exerts no influence, the particles move independently of each other, and we have the gaseous state.

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[*] Cooke.

[†] Dalton and Gay Lussac.

In the solid and liquid states the substances expand for an equal increment of temperature according to their co-efficient of expansion, which is a property of the mass; while in the gaseous state all substances behave alike, an equal increment of temperature producing in each case an equal increase in volume, because cohesion has ceased to act between the particles.

These particles, of which all matter is composed, and which have the same chemical and physical properties as the original mass, are called *molecules;* but when we investigate the composition of any compound mass, we find that these molecules, although they are ultimate particles as far as the particular substance is concerned, are built up of other kinds of elementary matter held together by chemical affinity.

For instance, a molecule of chalk is the smallest particle we can imagine to possess the properties of the mass; yet inasmuch as we can decompose chalk into quicklime and carbon dioxide, and these again into calcium, oxygen and carbon, it is evident that each molecule of the chalk must contain still smaller particles of these elements; and these smaller particles which go to build up the molecule we call *atoms.* We define the molecule as being the "smallest particle of matter which can exist free and still retain the properties of the mass, and these particles are always built up of two or more atoms."

The atom is the smallest particle which can exist in combination.

In order to facilitate the expression of chemical reactions, each of these elementary atoms is represented by a symbol consisting of the initial letter of its Latin name, or in case two or more elements commence with the same letter, the initial and first distinctive letter are used. For instance:

Sulphur is represented by S.
Silicon ,, ,, Si.
Strontium ,, ,, Sr.
Selenium ,, ,, Se.
Silver (Latin, Argentum) Ag.

Inasmuch as these Symbols stand for an atom of the element which they represent, we can, by experimentally determining the number of atoms of each element present in the molecule of a compound, represent symbolically the molecule by placing together the atomic symbols in the right proportion. We can by experiment prove that the molecule of chalk contains one atom of calcium (Ca), one of carbon (C), and three of oxygen (O), and the molecule can therefore be represented by CaCOOO; it would, however, be inconvenient to repeat the symbol for an atom when the same element occurs more than once, and we therefore express the number of the elementary atoms by placing a small numeral after and below them, so that the molecule of chalk would be written $CaCO_3$. A molecule of a substance so represented in symbols is called a Formula, and by experimentally determining the proportions in which substances react upon each other, we can by means of the formulæ build up a representation of the changes taking place.

When mercuric oxide is heated it breaks up into mercury and oxygen, and experiment shows us that these elements are combined, atom for atom, in the compound; hence the decomposition can be represented as

$$\overset{\text{Mercuric oxide}}{2HgO} = \overset{\text{Mercury}}{Hg_2} + \overset{\text{Oxygen.}}{O_2}.$$

The large numeral in front of the symbol for mercuric oxide multiplying the whole molecule, whilst the sign of addition between the mercury and oxygen shows that they are no longer in chemical combination. In the same way it is found by experiment that the molecule of sulphuric acid contains two atoms of hydrogen (H), one of sulphur (S), and four of oxygen (O), and that when this is acted upon by zinc (Zn), the zinc replaces the two atoms of hydrogen, forming zinc sulphate, and the two atoms of hydrogen (which constitute a molecule of hydrogen) escape free. This action we represent as:

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

Such a symbolical representation of a chemical change we call an *equation.*

By the careful consideration of various physical phenomena, it has been ascertained that the diameter of the molecules cannot be smaller than the fiftieth part of a micromillimeter, or larger than seven times this dimension.* It is therefore manifestly impossible to obtain any knowledge of the absolute weight of molecules or atoms, but we can in several ways determine the relative weights of dissimilar molecules and atoms.

The volume of all compound gases bears a simple ratio to the volumes of its gaseous constituents, for instance:

1 vol. hydrogen combines with 1 vol. chlorine and forms 2 vols. hydrochloric acid.

2 vols. hydrogen combine with 1 vol. oxygen and form 2 vols. steam.

3 vols. hydrogen combine with 1 vol. nitrogen and form 2 vols. ammonia gas;

and it is therefore evident that the number of molecules which is contained in any volume of a gaseous body, must stand in a simple relation to the number contained in the same volume of any other gas measured under the same conditions of temperature and pressure.

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* The micromillimeter is the millionth part of a millimeter.

In comparing or measuring gases it is absolutely essential that the temperature and pressure should be the same in each case, as the volume of a gas is increased by rise of temperature and diminished by pressure.

All gases expand to the same extent, for the same increase in temperature, provided the gas be at a temperature a few degrees above that at which it assumes the liquid state, and for each degree on the Centigrade scale through which the temperature of the gas is raised or lowered, it expands or contracts $\frac{1}{273}$ of the volume occupied at 0° C. (Law of Charles).

The Centigrade thermometer is always employed in scientific work, and differs from the Fahrenheit, in that the point at which water freezes is called "zero" in the Centigrade and "32°" on the Fahrenheit scale; and the boiling point on the former is 100, whilst in the latter 212. One scale can be readily converted into the other by the formulæ:—

$$\frac{5}{9}(\text{F.}^\circ - 32) = \text{C.}^\circ$$

$$\frac{9}{5}\text{C.}^\circ + 32 = \text{F.}^\circ$$

It is evident that if all gases expand $\frac{1}{273}$ of their volume starting from 0° C., that 273 volumes of a given gas, measured at 0° C., would become 274 at 1° C., 293 at 20° C., and the gas would have doubled its volume at 273° C.—hence, as all gases expand in an equal ratio, if we take:

$$\left.\begin{array}{l} v = \text{old volume} \\ v^1 = \text{new volume} \\ t = \text{old temperature} \\ t^1 = \text{new temperature} \end{array}\right\}\text{then} \quad v^1 = \frac{v \times (273 + t^1)}{273 + t}.$$

All gases behave alike under the influence of pressure, if experimented upon under conditions sufficiently far removed from their point of liquefaction; and it has been found that the volume of a gas varies inversely as the pressure brought to bear upon it; if the pressure be doubled the volume is reduced by one-half, and *vice versâ* (Boyle and Mariotte's law). The atmospheric pressure is measured by the barometer, in which a column of mercury is supported in a tube by the weight of the superincumbent air, and the normal height of mercury so supported is 30 inches, which approximately corresponds to 760 m.m., and as we express the barometric pressure in millimeters, it is evident that we can calculate the increase or decrease in volume due to barometric disturbance by a direct proportion.

Suppose a given volume of gas to be measured at a time when the barometer stood at 755 m.m., and that the pressure was increased to 768 m.m., the volume would decrease in the ratio of 768 to 755, or in other words:

$$\text{New vol.} = \frac{\text{old vol.} \times 755}{768}.$$

These variations in volume, due to change of temperature and pressure, have made it necessary to fix a standard temperature and pressure at which all gases shall be measured, and for all scientific purposes 0° C. and a barometric pressure equal to 760 m.m. of mercury have been adopted, and called the "normal" temperature and pressure.

Now it is evident that it would be practically impossible to secure these conditions, so that the usual method adopted is to measure the gas under ordinary circumstances, and having noted the temperature and pressure, to calculate what would be the volume under *normal* conditions of temperature and pressure, and this is done by the formula:

$$\frac{v\,p}{T} = \frac{v^1\,p^1}{T^1},$$

where—

v = original volume.
p = observed pressure.
t = observed temperature in (273 ∓ °C.).
v^1 = required volume.
p^1 = normal pressure.
t^1 = normal temp. (273 + 0°C.)

This formula is adapted for any calculation as to change in volume, etc., by using v^1, p^1, and t^1, as may be required.

This similar behaviour of gases under pressure (Boyle and Mariotte's law) and their equal rate of expansion with equal increments of temperature (law of Charles), suggest when taken in conjunction with the facts of the simple ratios by weight and by volume, in which gases combine, that as gases consist of little particles separated by equal distances (measured from the centres of the particles), and as heat or pressure will cause an equal increase or diminution of these distances, then it follows that equal volumes of all gases must contain an equal number of these particles; and this is formulated in the law of *Avogadro*, that "equal volumes of gases measured under the same conditions of temperature and pressure contain the same number of molecules."

It follows from the law of Avogadro, that the weights of two equal volumes of gases will stand to each other as the weights of their respective molecules, and in this way a relation can be established between the molecules of the gaseous elements and compounds.

It has been shown that a certain volume of oxygen weighs 16 times as much as an equal volume of hydrogen, hence if we called our molecule of hydrogen unity, the molecular weight of oxygen would be 16; but we have defined the molecule as consisting of two or more atoms, and we can prove that the elementary molecules of oxygen, hydrogen, and nitrogen, &c., consist of two atoms, so that if the hydrogen molecule were taken as one, the atoms would have to be represented by a fraction, which would be not only inconvenient but incorrect. Knowing, then, that the molecule of hydrogen contains two atoms, the atom of hydrogen is called unity and the molecule 2, and then as oxygen is bulk for bulk 16 times heavier than hydrogen, its molecular weight is said to be 16 × 2, or 32.

From this we can deduce the rule that "The atomic weight of a gaseous element is the ratio of its weight as compared with an equal volume of hydrogen as unity," and also the "molecular weight of a gas, elementary or compound, is its weight bulk for bulk compared with hydrogen as 2."

Now a compound gas cannot have an atomic weight, because it is built up of dissimilar atoms; but if we want to compare it volume for volume with hydrogen as unity, we must divide its molecular weight by 2, and the number so obtained is called its density—hence

$$\text{Density} = \frac{\text{Molecular weight}}{2}.$$

By far the largest number of the elements are not volatile, and therefore it is evident that the direct method of comparing the weights of equal volumes to find the atomic weight can only be used in a very limited number of cases, indeed it is more often used to check the atomic weights deduced from chemical considerations.

Many elements which are not themselves gaseous form gaseous compounds, so that the molecular weight of the compound can be ascertained, and the atomic weight is the smallest weight which enters into or is expelled from combination. For instance, carbon has never been volatilised, but it forms many gaseous compounds, which, on analysis, give:

	Carbonic acid.	Carbonic oxide.	Marsh gas.	Olefiant gas.
C	27.2	42.8	75	85.7
O	72.7	57.2	—	—
H	—	—	25	14.3
	99.9	100.0	100	100.0
Or, in	44 parts	28 parts	16 parts	28 parts.
C	12	12	12	24
O	32	16	—	—
H	—	—	4	4

Therefore 12 is taken as the atomic weight.

Where no gaseous compounds are known, then the atomic weight is determined by finding the weight which can combine with or displace one part of hydrogen or any element of known atomic weight; the number so obtained is called the equivalent of that element, and the atomic weight will either be that or a simple multiple of it. For instance, we find that when iron acts upon sulphuric acid 28 parts by weight of iron replace and turn out one part by weight of hydrogen, and we therefore say that 28 is the equivalent of iron, and the atomic weight will either be 28 or some simple multiple of that number; and this point is determined by taking advantage of the fact that a relation exists between the specific heats and the atomic weights of most of the elements, and which is embodied in Dulong and Petit's law, that

$$\text{Atomic weight} = \frac{6.4}{\text{Specific heat.}}$$

Water has a greater capacity for heat than nearly all other bodies.* If we take the amount of heat required to raise 1 lb. of water through 1° C. and call it 1, then the amount of heat required to heat the same weight of other substances through 1° C. will be less than 1, and this fraction is called the specific heat.

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* Dupré and Page [*Trans. R. S.* 1869] have shown that a mixture of alcohol and water containing 20% alcohol has a specific heat of 105, water=100.

On determining the specific heat of iron it is found to be .112 and $\frac{6.4}{.112} = 56$ or 28×2, therefore we say that 56 and not 28 represents the atomic weight of iron.

In a few cases the determination of the atomic weight has been influenced by the fact that identity of crystalline form indicates analogy of chemical constitution.

When compounds form crystals having the same form they are said to be "isomorphous," and in many cases the isomorphous bodies are found to be analogously constituted. This is well seen in the chlorides, iodides and bromides of sodium and potassium.

Having now seen that the atomic weights of the elements are ratios of weight deduced from actual experiment, it is evident that our symbolical representation of chemical reactions can be endowed with quantitative significance by building up from the atomic weights of the constituents the molecular weight.

The molecular weight of a compound is the sum of the atomic weights of the elements composing the molecule.

Considering the equation for the action of zinc on dilute sulphuric acid, we can by means of our atomic weights represent the proportions by weight in which the zinc and sulphuric acid react upon each other, and the weight of the new substances formed:

$$\begin{array}{ccccccc} \text{Sulphuric acid} & & \text{Zinc} & & \text{Zinc sulphate} & & \text{Hydrogen} \\ H_2SO_4 & + & Zn & = & ZnSO_4 & + & H_2 \\ \underbrace{2 + 32 + (16 \times 4)}_{98} & + & 65 & = & \underbrace{65 + 32 + (16 \times 4)}_{161} & + & 2 \end{array}$$

Molecular weight of H_2SO_4. Molecular weight of $Zn\,SO_4$.

No uniformity of nomenclature exists amongst the older elements, names having been given to them as they were discovered, and these old familiar names being in most cases retained. The more recently discovered metallic elements end in "um," as calcium, sodium, &c.

When two elements combine together, the name of the metal is written first, and the non-metal is given the termination "ide," as:—

Calcium combines with oxygen to form calcium oxide.

Sodium combines with chlorine to form sodium chloride.

Lead combines with sulphur to form lead sulphide.

When the same metal forms several distinct compounds with different proportions of the same non-metal, a prefix is added to the non-metal to signify the number of atoms of it present in the molecule.

An atom of lead forms with one atom of oygen—lead monoxide.

An atom of lead forms with two atoms of oxygen—lead dioxide.

When the metal and non-metal are present in the ratio of two atoms of the metal to three of the non-metal we use the prefix "sesqui":

Fe_2O_3 is iron sesquioxide.

When a metal forms two classes of compounds, one of which corresponds to a lower oxide, and the other to a higher, the lower class is distinguished by adding the suffix "ous" to the metal, whilst the higher class has the termination "ic"; for instance, we have:

Ferrous chloride and ferric chloride.

Mercurous iodide and mercuric iodide.

The nomenclature of the acids bears the impress of every change in chemical theory, but the present definition being that an acid is a compound containing replaceable hydrogen, the term acid will be applied to such bodies as HNO_3 nitric acid, $H_2 SO_4$ sulphuric acid, &c.

When two acids contain the same elements with a varying amount of oxygen, the one with less oxygen is distinguished by the termination "ous"; the other by "ic," for instance:

HNO_2 is called nitrous acid.
HNO_3 is called nitric acid.
H_2SO_3 is called sulphurous acid.
H_2SO_4 is called sulphuric acid.

When the hydrogen in an acid is replaced during chemical action by a metal, a compound called a salt is formed, and the salt formed from an acid with the termination "ous," is distinguished by the suffix "ite"; whilst the higher acid ending in "ic," forms salts ending in "ate":

Nitrous acid and sodic oxide give sodic nitrite and water.

$$2(HNO_2) + Na_2O = 2(NaNO_2) + H_2O.$$

Nitric acid and sodic oxide give sodic nitrate and water:

$$2(HNO_3) + Na_2O = 2(NaNO_3) + H_2O.$$

In all quantitative scientific work the French or metric system of weights and measures is used. A fixed standard, supposed to be $\frac{1}{10.000.000}$ of the distance from the pole to the equator, is taken, and this is called a meter—it is 39·37 inches long; and this meter is divided into ten equal parts called decimeters, or one hundred equal parts called centimeters. The weight of one cubic centimeter of water is called a gram and weighs about 15 grains, and 1,000 grams are called a kilogram.

The space occupied by 1,000 cubic centimeters, or 1,000 grams of water, is called a liter (a little under a quart).

Tables of the Metric System will be found in full in the Appendix, and also tables showing the relation between the English and French weights and measures.

In the following table the atomic weights of the Elements, according to the most recent and accurate determinations, are given in the first column, whilst in a second column will be found the whole numbers which have, for the sake of simplicity, been retained for all ordinary calculations.

Elements.	Symbol.	Atomic Weight.		Elements.	Symbol.	Atomic Weight.	
Aluminium	Al	27.0	—	Mercury	Hg	199.8	200.0
Antimony (Stibium)	Sb	119.6	—	Molybdenum	Mo	95.8	—
Arsenic	As	74.9	—	Nitrogen	N	14.01	14.0
Barium	Ba	136.8	137.0	Nickel	Ni	58.6	—
Beryllium	Be	9.1	—	Niobium	Nb	94	—
Bismuth	Bi	207.5	—	Osmium	Os	195	—
Boron	B	10.9	11.0	Oxygen	O	15.96	16.0
Bromine	Br	79.76	80.0	Palladium	Pd	106.2	—
Cadmium	Cd	111.7	112.0	Phosphorus	P	30.96	31.0
Cæsium	Cs	132.7	—	Platinum	Pt	194.5	—
Calcium	Ca	39.9	40.0	Rhodium	Ro	104	—
Carbon	C	11.97	12.0	Rubidium	Rb	85.2	—
Cerium	Ce	140.4	—	Scandium	Sc	44	—
Chromium	Cr	52.4	—	Selenium	Se	78.9	—
Copper	Cu	63.2	63.0	Silver (Argentum)	Ag	107.66	108.0
Chlorine	Cl	35.37	35.5	Silicon	Si	28	—
Cobalt	Co	58.6	—	Sodium (Natrium)	Na	22.99	23.0
Didymium	Di	142.3	—	Strontium	Sr	87.3	—
Erbium	Er	166	—	Sulphur	S	31.98	32
Fluorine	F	19	19.0	Tantalum	Ta	182	—
Gallium	Ga	69.8	—	Tellurium	Te	125	—
Gold (Aurum)	Au	196.2	—	Thallium	Tl	203.6	—
Hydrogen	H	1	—	Thorium	Th	232	—
Indium	In	113.4	—	Tin (Staunum)	Sn	117.5	—
Iodine	I	126.54	127.0	Titanium	Ti	48	—
Iridium	Ir	192.5	—	Tungsten (Wolfram)	W	183.6	—
Iron (Ferrum)	Fe	55.9	56.0	Uranium	Uu	239	—
Kalium (Potassium)	K	39.03	39.0	Vanadium	Vv	51.2	—
Lanthanium	La	138.2	—	Ytterbium	Yb	173	—
Lithium	Li	7	—	Yttrium	Y	89	—
Lead (Plumbum)	Pb	206.4	207.0	Zinc	Zn	65.1	65.0
Magnesium	Mg	23.9	24.0	Zirconium	Zr	90	—
Manganese	Mn	54.8	—				

CHAPTER II.

HYDROGEN.

Preparation—Properties—Weight—Effect upon Sound—Solubility—Diffusion of Gases—Metallic properties of Hydrogen—Dual nature of the Hydrogen Molecule—Equality in volume of Molecules—Relation between weight and volume in Gases—Valency of Elements and Radicles.

IT has been shown that water can be decomposed into, or built up from, two gaseous constituents, hydrogen and oxygen, and the properties of these gases will now be considered.

Hydrogen.—This gas is only very rarely found free in Nature, sometimes occurring in the emanations from volcanoes, and in meteorites. Spectroscopic investigations, however, show that it is present in large quantities in the atmosphere of the sun. In combination it forms $\frac{1}{9}$ by weight of water, and also occurs in ammonia, sulphuretted hydrogen, and in all animal and vegetable tissues.

Hydrogen was known to the alchemists under the name of "inflammable air," but it was not until 1766 that its properties were fully examined by Cavendish.*

The gas is most conveniently prepared for experimental purposes by acting upon dilute sulphuric acid with the metal zinc; for this purpose zinc, which has been granulated by pouring it into water whilst molten, thus increasing the surface, is placed in the two-necked bottle (A, Fig. 6), and water enough to cover the metal is then poured in, sulphuric acid being added a few drops at a time by means of the thistle funnel (B) which passes, gas-tight, through a cork fitting the neck of the bottle and terminates below the surface of the liquid. The addition of the acid causes an immediate evolution of gas which is conducted by the leading tube (C) below the surface of water in the pneumatic trough (D), where it can be collected in cylinders by the displacement of water. The first portions of gas which escape must not be collected, being an explosive mixture of hydrogen and the oxygen of the air which originally filled the generating bottle.

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* *Phil. Trans.*, 1766, p. 144.

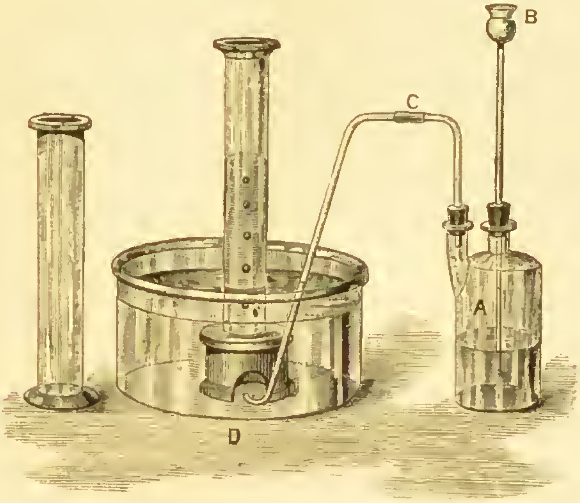

Fig. 6.

The reaction which takes place may be represented by the equation already used as a type, viz. :—

$$\overset{\text{Zinc}}{Zn} + \overset{\text{Sulphuric acid.}}{H_2SO_4} = \overset{\text{Zinc sulphate}}{ZnSO_4} + \overset{\text{Hydrogen.}}{H_2}.$$

In its physical properties hydrogen is most unmistakably non-metallic, but in all its chemical relations with other elements it behaves so like a metal that in considering the reactions in which it takes part we look upon it as one. In the preparation of hydrogen from zinc and hydric sulphate, we have the hydrogen atoms turned out of their combination with the sulphur and the oxygen by the chemically stronger metal zinc. In the same way we can replace the hydrogen in water by certain other metals; which, combining with the oxygen, set free the gaseous hydrogen. If we pass steam, the vapour of water, over iron heated to a dull red heat, the iron combines with the oxygen, forming an oxide of iron, whilst the hydrogen escapes free. This interchange of metals we may represent by the equation :

$$\overset{\text{Water vapour}}{4[H_2O]} + \overset{\text{Iron}}{3Fe} = \overset{\text{Black magnetic oxide of iron}}{Fe_3O_4} + \overset{\text{Hydrogen.}}{4(H_2)}.$$

This method of obtaining hydrogen is perhaps the cheapest and best when large quantities of the gas are required.

Some metals like iron have the property of decomposing water at a red heat; others, like sodium and potassium, break it up at ordinary temperatures; whilst gold and silver are unable to decompose it at all.

If sodium is placed in contact with water a violent action takes place, one-half of the hydrogen of the water is liberated, the sodium combining with the remainder of the hydrogen and the oxygen to form sodic hydrate :

$$\overset{\text{Sodium}}{Na_2} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Sodic hydrate}}{2[Na\,HO]} + \overset{\text{Hydrogen.}}{H_2}.$$

The same chemical reaction takes place when potassium is thrown on water, but in this case the heat generated by the combination of the metal with the oxygen and part of the hydrogen is so great that the escaping gas is set on fire.

$$\overset{\text{Potassium}}{K_2} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Potassic hydrate}}{2[KHO]} + \overset{\text{Hydrogen.}}{H_2}.$$

In these two cases only half the hydrogen contained in the water is liberated, but if the sodic hydrate or potassic hydrate be again acted upon with excess of sodium or potassium, the remaining atom of hydrogen is turned out.

$$\overset{\text{Sodic hydrate}}{2[NaHO]} + \overset{\text{Sodium}}{Na_2} = \overset{\text{Sodic oxide}}{2(Na_2O)} + \overset{\text{Hydrogen.}}{H_2}.$$

By which ever method prepared, hydrogen, when pure, is a colourless gas, without taste or odour; it has no poisonous action on life, and may be breathed for a few moments, but will destroy life when inhaled for any length of time by excluding the oxygen of the air, required for respiration, from the lungs.

Hydrogen has no action on test papers or lime water; it does not support combustion, but itself burns in contact with oxygen with a non luminous, but intensely hot flame, water being the only product of its combustion.

In burning it produces a greater heat than the same weight of any other known substance—1 lb. of hydrogen in combining with 8 lb. of oxygen giving out sufficient heat to raise 34,462 lb. of water 1° C.

All gases, with the exception of hydrogen, have been condensed to a liquid by cold or pressure, or the two combined; and it has been lately shown by Wroblewski, that hydrogen even when subjected to a pressure of 110 atmospheres and at the same time cooled to a temperature of —213.8 °C., shows no sign of liquifaction.

Hydrogen is the lightest body known, being 14.47 times lighter than air, hence it is taken as the standard with which the weight of all other gases is compared. The ratio by weight which a gas bears to an equal volume of hydrogen is called its density—hence, when we say that the density of oxygen is 16, we mean that any volume of oxygen will weigh 16 times as much as the same volume of hydrogen measured under similar conditions of temperature and pressure.

Sound will travel three times as fast as hydrogen as in air; but sounds generated in hydrogen are rendered so feeble as to be hardly audible when transmitted to air.

This may be shown by mounting an electric bell (B, Fig. 7) in an open gas jar (A) and while it is ringing, passing in hydrogen gas by the tube (C) from a reservoir of compressed gas. Hydrogen, being so much lighter than air, will collect at the top of the jar and surround the bell, causing the sound to almost entirely disappear, and if now the supply of gas is cut off, and the cork of the exit tube (E) be removed, the hydrogen will escape and the original intensity of the sound restored.

Temperature has an effect upon the solubility of most gases; less being dissolved as the temperature rises, but 100 volumes of water will dissolve 1.93 volume of hydrogen without reference to temperature.

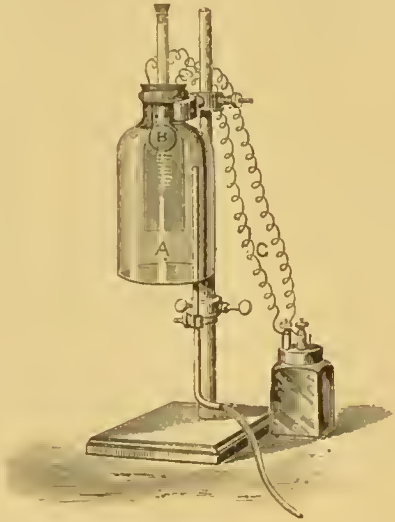

Fig. 7.

Hydrogen being 14.47 times lighter than air, renders the gas of value for filling balloons; but it is only used for this purpose when a rapid ascent to a great altitude is required, as it has the property of very rapidly escaping from the vessel which contains it if there be the slightest leak; so that when a prolonged ascent is desired it is preferable to fill the balloon with ordinary coal gas which, although it has not so great a lifting power, does not escape so rapidly. The escape of hydrogen is due to a property which gases possess of mingling together against the force of gravity, so that heavy and light gases tend to become evenly mixed, a property which is of the greatest importance in the economy of Nature. This action, which is called "diffusion," takes place more slowly in the case of heavy gases than light ones, and experiment has shown that the "rate of diffusion" varies with the density of the gases. "Gases diffuse into one another at a rate which is inversely as the square roots of their densities." Hence, if a vessel of hydrogen be connected with a vessel of oxygen by means of a pin-hole—the square root of 1 (density of hydrogen) being 1, and the square root of 16 (density of oxygen) being 4—4 volumes of hydrogen will pass through into the oxygen during the first moment of time, whilst only 1 volume of oxygen will pass into the hydrogen, with the result that the pressure will be increased in the vessel containing the

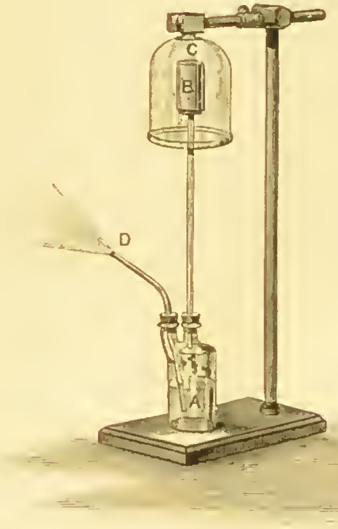

Fig. 9.

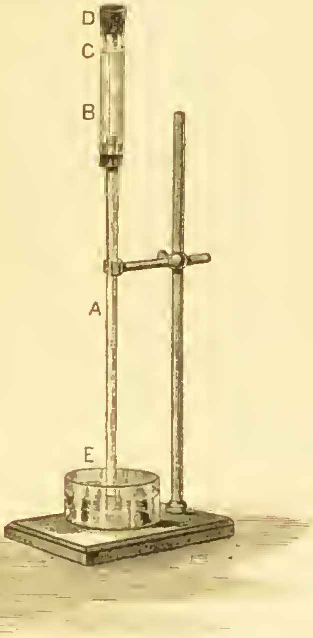

Fig. 8.

oxygen, but will be decreased in that originally containing the hydrogen.

If a tube (A, Fig. 8) be connected with one of wider bore (B), which is closed an inch from the top by a porous plug of plaster of Paris (C) and closed above the plug by an india-rubber cork (D), diffusion through the plug may be shown by filling the tube with hydrogen, standing it in some coloured liquid (E) and removing the cork (D).

At once a rise of the liquid in the tube (A) takes place, showing that the hydrogen gas is diffusing out into the air faster than the air diffuses into the hydrogen, with the result that a reduction of pressure takes place in A and B, and water in consequence rises in the tube A. The same thing may be shown in the reverse way by the apparatus shown in Fig. 9. A two-necked bottle (A) is fitted with a tube ending in a porous earthenware vessel such as is used in a galvanic cell (C). Over this a bell jar (C) containing hydrogen gas is placed, and the hydrogen diffusing in faster than the air can diffuse out, causes an increase of pressure on the surface of the liquid in A, and drives some of it out from the jet D.

Although the physical properties of hydrogen are opposed to the idea of its possessing metallic properties, yet its chemical behaviour points so strongly to this conclusion that it is now generally looked upon as being the vapour of a metal. In the first place, when we decompose a solution of a metallic salt by means of a galvanic current, we always find that the metal is liberated at the negative pole, or where the current leaves the liquid; and on decomposing water, rendered a conductor of electricity by addition of a few drops of sulphuric acid, we find that the hydrogen is liberated at the negative pole, that is, at the pole at which metals are always set free. Again, certain metals have the power of absorbing large quantities of hydrogen, and having absorbed it, they are found to have changed their physical properties, which points to the hydrogen having formed an alloy with them. The metal Palladium at ordinary temperatures absorbs no less than 376 times its own bulk of the gas, the alloy so formed being called Hydrogenium.

If a palladium wire, 2 ft. 6 in. long, be so arranged (Fig. 10) that it forms the negative pole in a galvanic circuit, with a large glass tube as a decomposing cell (A) and a platinum wire as the positive pole, on decomposing acidulated water hydrogen gas will be evolved on the surface of the palladium, and being occluded will cause an increase in length of the wire, which will be made visible by the lever arm (B).

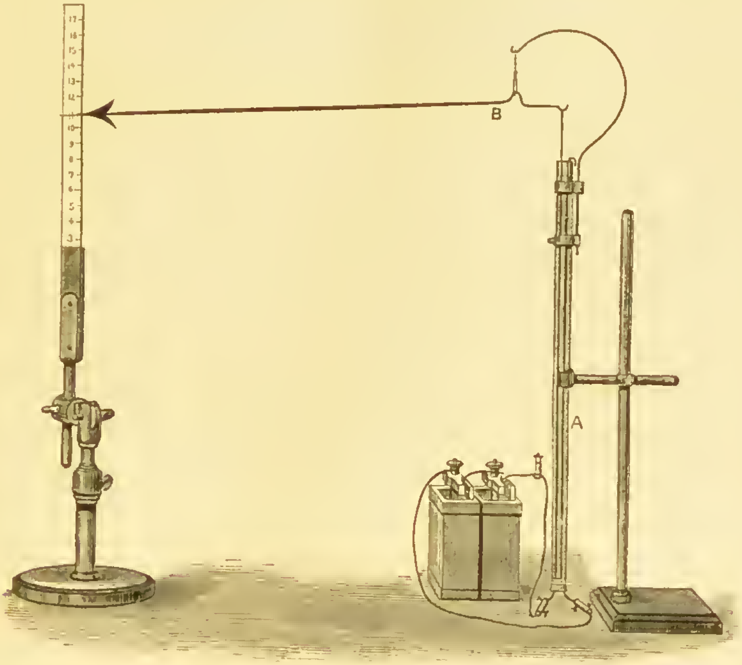

Fig. 10.

Finally, hydrogen, under certain thermal conditions, will replace many metals in compounds; whilst, under others, metals will take the place of hydrogen when they are brought in contact with compounds containing it. For instance, when hydrogen is passed over heated oxide of iron, the hydrogen replaces the iron—metallic iron is left and the hydrogen unites with the oxygen to form water—whilst when zinc is acted upon by hydrochloric acid, the zinc turns out the hydrogen, which escapes free and zinc chloride is the resulting compound.

According to Avogadro's law, equal volumes of gases contain an equal number of molecules, and it is therefore evident that molecules, or at any rate molecules with their particular share of intermolecular space, must all occupy the same volume. We may look upon an atom as occupying one volume, and we have defined the molecule as built up of two or more atoms; but whether it be built up of 2 or 200 atoms, if it be a gas, the molecule will always occupy the same space. It is therefore important to prove that the molecule of our standard gas, hydrogen, really consists of two atoms, as if we once prove this, we can prove that all gaseous molecules will occupy the same space as two atoms of hydrogen.

The molecules of all gases have the same properties and behave in the same way as larger volumes of the same gas; and this being the case, and equal volumes of gases containing the same number of molecules, it is evident that we can take equal volumes of two dissimilar gases and look upon the decompositions and general behaviour of the masses as being the behaviour of the molecules which build up the masses.

If we take a pint of carefully purified hydrogen gas we know that it contains nothing but hydrogen, whilst if we take a pint of hydrochloric acid gas it is easy to prove it contains one-half hydrogen and one-half chlorine.

This can be done by mixing together half a pint of pure chlorine and half a pint of pure hydrogen, when, by exposing them to diffused daylight, they will gradually combine to form one pint of hydrochloric acid gas, no alteration in volume taking place. It can also be proved by confining a known volume of hydrochloric acid gas over mercury in a bent tube (A, Fig. 11), and passing up into it a pellet of potassium on the end of a platinum wire (B). The potassium at once commences to absorb the chlorine of the hydrochloric acid gas, combining with it to form potassic chloride; and if the potassium be gently heated by a spirit-lamp flame to prevent any absorption of hydrogen, exactly half the gas will disappear, leaving only pure hydrogen behind. Another

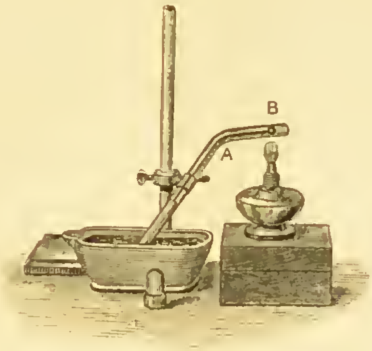

Fig. 11.

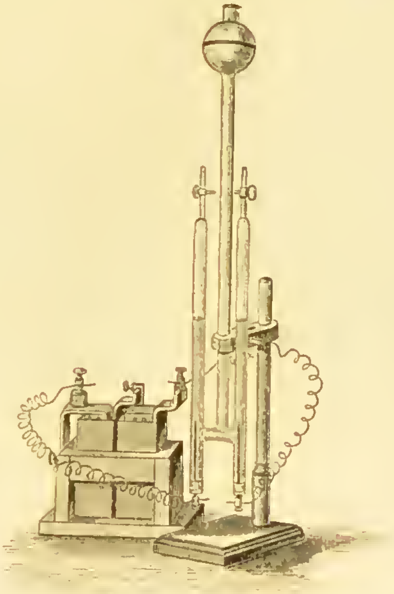

Fig. 12.

proof is that if saturated hydrochloric acid solution is decomposed by a galvanic current in a Hofmann's electrolytic apparatus (Fig. 12), using carbon electrodes, equal volumes of hydrogen and chlorine will be evolved.

It is therefore clear that our pint of hydrochloric acid gas is one-half chlorine and one-half hydrogen; and as each molecule has the same composition as the mass of which it forms part, each molecule of hydrochloric acid gas will be half chlorine and half hydrogen. It is also evident that the pint of hydrogen contains twice as much of that element as the pint of hydrochloric acid gas, so that each molecule of hydrogen will contain twice as much hydrogen as each molecule of hydrochloric acid gas.

We do not yet know, however, whether our molecule of hydrochloric acid contains one atom of hydrogen combined with one of chlorine, or two atoms of each; all we know is that they are equal in number.

Bodies like hydrochloric acid, have the property of combining with metals to form the class of substances we call salts; and if a metal like potassium or sodium be taken, the hydrogen which the molecule contains can be replaced by the metal, an atom at a time, so that if the molecule contains one atom only, it is all replaced at once; if two atoms, then it can be replaced in two separate stages, and so on for any number of atoms. Now in hydrochloric acid we can only replace the hydrogen in one operation, which proves that the molecule contains one atom of hydrogen and therefore one atom of chlorine, and as the molecule of hydrogen contains twice as much, it will contain two atoms.

It being thus proved that the molecule of hydrogen contains two atoms, as one atom occupies one volume we can say that the molecule will occupy two volumes, and as all molecules occupy the same space, all molecules will occupy two volumes, no matter how many atoms they may contain.

That this is really the case, is proved by the fact that when two gases combine to form a third, if more than an atom volume of one combine with an atom volume of another, there is a contraction, and the resulting gas occupies the space of two atom volumes ; for instance :—

1 vol. hydrogen combines with 1 vol. chlorine and forms 2 vols. hydrochloric acid gas.

2 vols. hydrogen combine with 1 vol. oxygen and form 2 vols. steam.

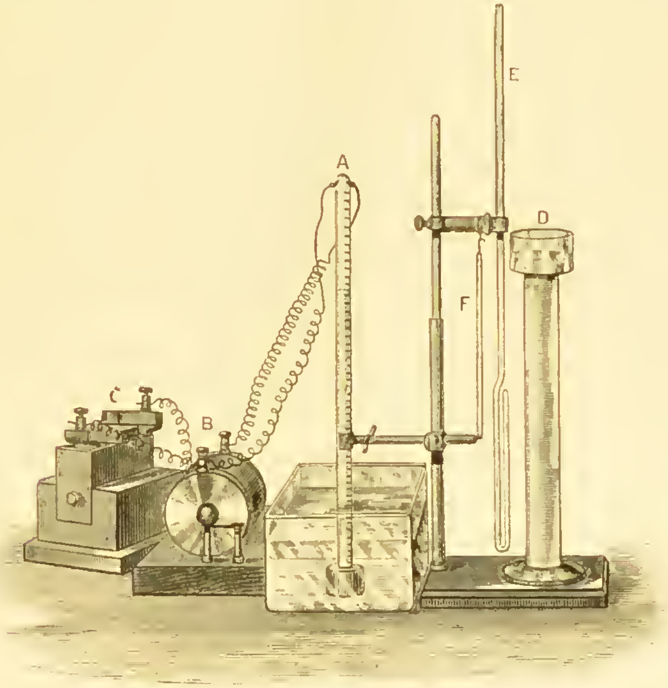

Fig. 13.

3 vols. hydrogen combine with 1 vol. nitrogen and form 2 vols. ammonia gas.

4 vols. hydrogen combine with 1 atom carbon and form 2 vols. marsh gas.

This can be proved experimentally as has already been done in the case of hydrochloric gas.

The proportions of hydrogen and oxygen in water can be accurately determined by eudiometric analysis. For this purpose we take a strong, accurately graduated glass tube (A, Fig. 13), open at one end and closed at the other, whilst through the closed end two platinum wires are fused, which terminate $\frac{1}{8}$rd of an inch apart inside the tube, and which can be connected with the poles of an induction coil (B) connected with the battery (C).

The tube is first filled with water, and is then inverted mouth downwards in a trough, also filled with water; hydrogen gas is then allowed to enter, and the volume it occupies is read off (say 100 volumes); oxygen is next passed in and the volume of mixed gases is noted (say 175). The tube is then pressed down upon a piece of flat indiarubber placed under the water, in order to prevent the sudden expansion due to heat (when combination takes place) blowing any of the gases out of the tube. An electric spark is now passed through the mixed gases by means of the platinum wires fused through the glass. A flash is seen to pass down the tube, showing that combination has taken place; and the water formed is deposited as dew on the sides of the tube and only occupies about $\frac{1}{2000}$ part of the bulk of the gases forming it. When the eudiometer is raised from the indiarubber pad the water rises in the tube and only 25 volumes of gas remain, and this is found to be pure oxygen.

Now the oxygen originally added was 175 − 100 or 75 volumes, 25 of which remain unused.

Thus we see that 100 volumes of hydrogen require exactly 50 volumes of oxygen for their complete combustion. In reading the quantities of gases contained in the eudiometer it is necessary to sink the tube in water until the level of the water inside the tube is the same as that on the outside, and this is done in the well (D).

Having thus proved that two volumes of hydrogen combine with one volume of oxygen to form water, we can repeat the experiment, using, however, a different shaped eudiometer and jacketing it with a glass tube through which the vapour of some liquid having a higher boiling point than water can be passed, so as to keep the water formed in the condition of steam. (Fig. 14.)

To do this the eudiometer (A) is surrounded by a wide glass tube (B); exactly two volumes of hydrogen and one of oxygen are placed in the eudiometer over mercury, and amyl alcohol (fusel oil) which boils at 128° C., is then vaporised in the flask (C), and is passed through the outer tube (B), and is condensed in the worm (E). This heats the gases and mercury in the eudiometer to a temperature several degrees above the boiling point of water, and if a spark is now passed through the mixed gases, a contraction exactly equal to one-third of the volume takes place, that is to say, the three atom volumes, in combining to form a molecule,

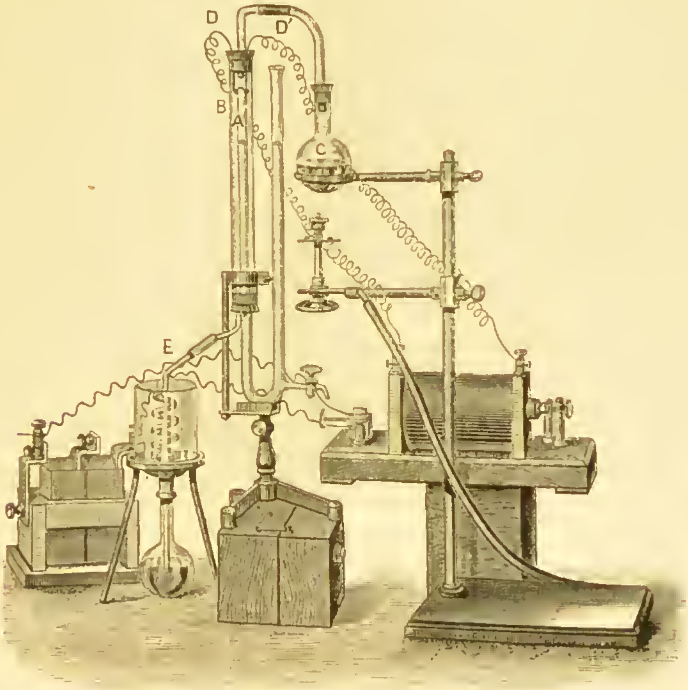

Fig. 14.

have contracted to the volume occupied by two atom volumes of hydrogen.

The same may be proved in the case of ammonia gas by collecting a known volume of it over mercury in the eudiometer tube (A, Fig. 15) and passing through it a series of electric sparks from the induction coil which decomposes the ammonia gas into its constituents, nitrogen and hydrogen, and cause it to double its volume.

$$\begin{array}{ccccc} \text{Ammonia gas} & & \text{Nitrogen} & & \text{Hydrogen} \\ \text{4 vols.} & & \text{2 vols.} & & \text{6 vols.} \\ 2(NH_3) & = & N_2 & + & 3H_2 \end{array}$$

and therefore four atom volumes of the nitrogen and hydrogen contract to two atom volumes when they combine to form the molecule of ammonia gas.

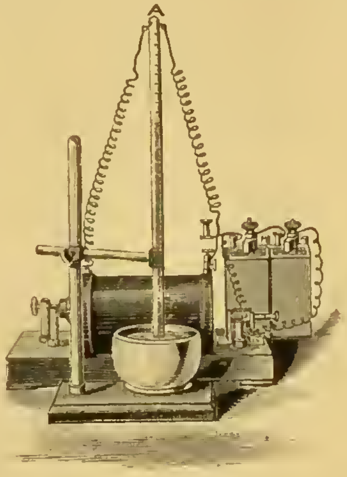

Fig. 15.

It has been already shown that the atomic weight of a gaseous element is the ratio of its weight volume for volume compared with hydrogen as unity, and that the molecular weight of a gas, elementary or compound, is its weight, volume for volume, compared, with hydrogen as two. If now we take a definite weight of hydrogen as representing an imaginary atom and determine the volume which this weight represents we can establish a relation between weight and volume which will be true for all gases. The gram being the unit of weight in all scientific work, we choose one gram of hydrogen as the imaginary hydrogen atom, and on measuring the volume of one gram of hydrogen under normal conditions of temperature and pressure (0°C and 760 mm.), we find that it occupies 11.16 liters, and this volume we take as our atom volume.

In the same way, two grams of hydrogen occupy 2 (11.16) liters, or 22.32 liters, and this we take as our imaginary molecule measure for gaseous elements and compounds; and can now formulate the two following laws:

1. "If the units in the atomic weight of any gaseous element be called grams, that number of grams will occupy 11.16 liters at 0° C., and 760 mm. pressure.
2. "If the units in the molecular weight of any gaseous element or compound be called grams, that number of grams will occupy 22.32 liters at 0°C., and 760 mm. pressure."

We now find our Chemical equation has a new significance, as if we call our atomic weights grams, then we can at once see not only the weight, but the volume of gas evolved in any chemical reaction.

$$\begin{array}{ccccccc} \text{Sulphuric acid} & & \text{Zinc} & & \text{Zinc sulphate} & & \text{Hydrogen} \\ H_2SO_4 & + & Zn & = & ZnSO_4 & + & H_2 \end{array}$$

98 grams + 65 grams = 161 grams + 2 grams or 22.32 liters.

In this equation, an atom of the metal zinc takes the place of two atoms of hydrogen, whilst if we acted upon the sulphuric acid with the metal sodium we should find that an atom of sodium could only replace one atom of hydrogen.

It is evident from this, that although the symbol of an element represents an atom of an element, the atom having an unchangeable relative weight, yet such a symbol does not represent the power which an element possesses of combining with or replacing other elements.

In hydrochloric acid we find one part by weight of hydrogen combined with 35.5 parts by weight of chlorine, and these being in the ratio of their atomic weights, and having proved that the molecule of HCl only contains one atom of hydrogen, we say that hydrogen combines atom for atom with chlorine to form hydrochloric acid. In the same way H combines atom for atom with bromine, iodine and fluorine, and these combine atom for atom with sodium, potassium and silver; hence we say that these elements have the same combining power as hydrogen, and when they unite together or replace each other in compounds, do so atom for atom; and this property we express by saying that they have the same atomicity or valency.

Turning to other elements, we find one atom of sulphur or oxygen unites with two atoms of hydrogen—that is, has double the combining power; whilst one atom of zinc will replace two atoms of hydrogen in a compound like sulphuric acid, and will combine atom for atom with sulphur or oxygen; such elements we say are "Dyads" or "Divalent"—that is, have the power of combining with, or replacing two atoms of, such elements as hydrogen, which are called "Monads" or "Monovalent." When elements combine with, or replace. three atoms of hydrogen, they are "Triads" or "Trivalent;" four atoms, "Tetravalent;" five atoms, "Pentavalent," and so on.

In this way all the elements may be arranged according to the number of atoms of hydrogen which represent their combining or replacing value, and if we do this, we find that in several cases the valency of an element varies, but this variation always manifests itself in the disappearance of an even number of combining values.

Arranging all the commoner elements according to their valency, we obtain the following table:—*

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* It is very doubtful if there is any absolute measure of atomicity, and any such grouping must be open to many exceptions.

I. Monads	II. Dyads	III. Triads	IV. Tetrads	V. Pentads	VI. Hexads
H	O	Bi	Pt	N	Al_2
Na	Ba	As	Sn (ic)	P	Cr_2(ic)
K	Sr	Sb	C		Fe_2(ic)
Am	Ca	Au			Mn_2(ic)
Ag	Mg	N			S
Cl	Zn				
Br	Ni				
I	Co				
F	Cd				
	Cu				
	Hg (ic)				
	Hg_2(ous)				
	Fe (ous)				
	Mn (ous)				
	Sn (ous)				
	S				
	C				

If we take sulphuric acid and act upon it with sodium or potassium, we find that we can replace the hydrogen which it contains atom for atom, and we can do this in two separate stages; showing that the molecule of H_2SO_4 contains two atoms of hydrogen in its composition, which can be replaced by two atoms of a monad or one atom of a dyad element.

The group of atoms (SO_4) which the sulphuric acid contains, is found present in all sulphates, and is in fact the distinctive feature of this class of salts—it cannot exist by itself, it must be in combination with some metallic element or elements, and these can be changed, whilst the SO_4 remains constant in the compound. Now a group of atoms which can theoretically in this way be moved as a whole from one compound to another is called a compound radicle, and as this radicle will combine with two atoms of hydrogen, it is evident that it is a dyad.

All the acids contain in this way an atom or group of atoms, which form the distinctive feature of the particular class of salts derived from them, and is called the acid radicle of the salt, and having experimentally determined how many atoms of replaceable hydrogen there are in the hydrogen salt (the acid) we can arrange the acid radicles according to their valency.

	I. Monads		II. Dyads		III. Triads
$-Cl$	Chlorides	$=O$	Oxides	$\equiv PO_4$	Phosphates
$-Br$	Bromides	$=S$	Sulphides	$\equiv BO_3$	Borates
$-I$	Iodides	$=SO_3$	Sulphites		
$-F$	Fluorides	$=SO_4$	Sulphates		
$-CN$	Cyanides	$=CO_3$	Carbonates		
$-HO$	Hydrates	$=CrO_4$	Chromates		
$-NO_2$	Nitrites	$=SiO_3$	Silicates (meta)		
$-NO_3$	Nitrates				IV. Tetrads.
$-ClO$	Hypochlorites			≣ SiO_4	Silicates
$-ClO_3$	Chlorates				(ortho)

In this table only the more ordinary radicles are given, and it is necessary to remember that cases will occur in which it is impossible to build up the molecular formula of a compound from any such tables.

CHAPTER III.

CHEMISTRY OF THE GALVANIC BATTERY.*

Heat of chemical action converted into galvanic electricity—"Polarisation"—Arrangements adopted in various cells—Chemical action taking place in the "Daniell"—"Varley-Daniell"—"Menotti-Daniell"—"Leclanché"—"Grove"—"Bunsen"—"Bichromate" and secondary cells—Electrolysis—Electrolytes—Electro-metallurgy—Importance of the Electro-chemical relations between metals on ships' bottoms—Muntz-metal—Zinc protectors—Zinc sheathing—Mooring vessels.

NO chemical change can take place without being accompanied by a physical change, and the most ordinary physical manifestation accompanying chemical action is change of temperature.

For instance, when we acted upon dilute sulphuric acid with zinc, hydrogen gas was rapidly evolved, zinc sulphate was formed and considerable heat generated. The heat so generated may be used to boil ether or alcohol, and the vapour so generated might be made to do mechanical work, in the same way that the heat generated by burning coal may be made to boil water, and the steam then used for driving an engine—so converting the heat of chemical combination, a form of energy, into mechanical work. In this way one form of energy can be translated into other forms of energy; but, like matter, energy cannot be created or destroyed.

When zinc decomposes sulphuric acid, energy is developed as heat, the energy being due to the rearrangement of the atoms in the sulphuric acid and the zinc, and, by proper arrangements, we can convert this heat into electricity.

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* In describing the action taking place in the various cells, the explanations employed in the first volume of the *Torpedo Manual* have been adopted so as to avoid any confusion.

Instead of taking granulated zinc, take a sheet of zinc and place it in the dilute acid; the same action as before takes place, hydrogen is generated on the surface of the zinc and the zinc slowly dissolves as zinc sulphate; now place a sheet of copper in the acid but not touching the zinc, the action continues as before; but now allow the copper to touch the zinc either below or above the surface of the liquid, or connect the two plates of dissimilar metal by a wire, the evolution of hydrogen on the surface of the zinc plate diminishes, and gas now appears on the copper plate.

If the plates be weighed before and after the action, the weight of the copper plate will be found to be unchanged, whilst the zinc will have lost weight, and, on testing the acid, it will be found to contain large quantities of zinc sulphate in solution, showing that the zinc has continued to dissolve although the hydrogen has been coming off on the copper plate. If the wire which connects the two plates when in the acid solution be now examined, it will be found to possess properties it did not before, and if cut in the centre and one end be placed above the tongue and the other end under the tongue, a peculiar sensation and strong metallic taste will be experienced; whilst if several such couples of zinc and copper be placed in vessels full of dilute acid, and the zinc of one be connected with the copper of the next, and so on, the two terminals being as before connected with a wire, a strong galvanic current will be found to be flowing through the wire, and if the wire be held over and parallel to a magnetic needle, the needle will be deflected and will tend to stand at right-angles to the wire, instead of pointing N. and S.

The current so produced, however, will soon diminish in strength, and will eventually cease.

If we examine the thermal conditions existing in the interior of the cell, we find that although we get heat given off by the solution of zinc in sulphuric acid under ordinary conditions, yet when the zinc is dissolved in contact with a copper plate and a galvanic current is produced, the generation of heat diminishes in the cell, although the zinc dissolves more rapidly, that is, the heat which is generated by the chemical action is converted into another form of energy, viz., electricity, and will again be converted into heat wherever resistance occurs.

In the creation of the electric current, or more properly speaking, the conversion of the heat of chemical combination into electricity, we have now to explain the fact that when the current is produced, the hydrogen ceases to be evolved on the surface of the zinc and appears instead upon the copper plate.

We may imagine that the molecules of H_2SO_4 are as it were magnetised when the current is set up, and place themselves in rows, the acid radicle SO_4 in the molecule next the zinc, whilst the H_2 is turned towards the SO_4 of the next molecule, and so on until the copper plate is reached, when we find that the H_2 is in contact with it. When the zinc dissolves, the molecule of H_2SO_4 in contact with it gives its SO_4 to the zinc forming $ZnSO_4$, whilst the H_2 instead of being given off free, unites with the SO_4 of the next molecule of H_2SO_4, and so combination of H_2 with the next SO_4 takes place throughout the whole chain of molecules until the copper is reached, when the last H_2 has nothing to combine with and so is liberated on the surface of the copper. In order to create an electric current we must have two dissimilar metals, one having a greater affinity for the $=SO_4$ radicle than the other, in order to affect the arrangement of the molecules necessary for the passage of the current. If we used two plates of zinc some of the molecules of H_2SO_4 would have their SO_4 radicles towards one plate and some towards the other, the result being generation of H_2 at both plates, the evolution of heat and no electricity.

The greater the difference in the attraction for SO_4 of the two metals used, the stronger the current produced—for instance, if iron and zinc be taken, the zinc has a stronger affinity for SO_4 than the iron, but as the iron has also affinity for SO_4, the strength of the current formed will be represented by the affinity of the zinc less the affinity of the iron; whilst if zinc and platinum or zinc and copper be used, the platinum and copper having little or no affinity for the SO_4, a much stronger current is produced.

All our batteries are dependent upon some such action as the solution of zinc in hydric sulphate for the production of electricity, and the chief differences in the forms of the batteries used consist of devices for maintenance of the current.

We have seen that commercial zinc placed in diluted sulphuric acid rapidly dissolves under ordinary circumstances; but if we use perfectly pure zinc and perfectly pure diluted sulphuric acid, no solution of the zinc or other action takes place until the second metal is introduced and brought in contact with it; hence it is evident that the purer the zinc and the purer the acid, the smaller the quantity that will be used up in the intervals when the battery is not in action. Perfectly pure zinc is not easy to obtain, but if we rub a clean surface of the metal with mercury, the mercury dissolves the pure zinc and forms what we call an amalgam, and in this way only the pure metal is presented to the action of the acid, and the minimum amount is used up when the battery is not at work, all local action being done away with. We saw that when a galvanic current was produced by a sheet of zinc and a sheet of copper immersed in dilute sulphuric acid, ~~that~~ the current rapidly diminished in strength, a result partly due to the hydrogen liberated collecting on the copper or platinum plate and so opposing more and more resistance to the current, and also to the hydrogen setting up a counter electro-motive force, ~~and~~ in all forms of battery in ordinary use various devices are adopted to prevent this so called "Polarisation of the plate."

The hydrogen acts in three ways in weakening the current: (1) being a non-conductor of electricity, the more hydrogen there is present, the more will the surface of the copper or platinum be reduced in size and therefore the smaller will be the acting surface; (2) the freshly liberated (nascent) hydrogen deposited on the surface of the copper being electro-positive to zinc will set up a current in the reverse direction of the original one; (3) when much sulphate of zinc is present in the solution, the nascent hydrogen tends to decompose it, and a deposit of zinc is formed on the copper, so that we practically have two plates of zinc opposing each other instead of a plate of zinc and a plate of copper.

The usual method employed for getting rid of the hydrogen is to surround the copper or platinum plate with some substance with which the hydrogen can combine and so prevent its deposition.

In the "Daniell" and the "Varley-Daniell" this is done by separating the cell into two parts by a porous partition, placing in one the zinc and dilute sulphuric acid, and in the other the copper in a saturated solution of copper sulphate: the two liquids meet in the pores of the partition, but otherwise only mingle very slowly. The zinc is dissolved by sulphuric acid with formation of zinc sulphate, and nascent hydrogen coming off at the copper plate, being evolved in presence of sulphate of copper, reduces it, forming sulphuric acid and depositing pure copper on the copper plate, the deposit tending rather to increase the current than otherwise.

In this way the current is rendered much more constant, but in spite of the porous partition, whether formed of unglazed earthenware or fearnought, there will always be a tendency on the part of the sulphate of copper solution and sulphate of zinc to mingle, and when the sulphate of copper reaches the zinc plate, then copper is deposited on the zinc and at once weakens the current.

The current generated in a Daniell's cell is rarely as strong for the first few minutes as that generated by a single liquid cell, as the decomposition of the sulphate of copper by the nascent hydrogen uses up a certain amount of chemical energy, and tends to create a current in the opposite direction, so that it is only the difference between the two forces that we can utilise as a current; the various forms of the Daniell cell are therefore used where a continuous and constant current is required.

The "Menotti-Daniell," used for testing purposes, consists of an ebonite or glazed earthenware vessel, at the bottom of which is a tray of copper half-an-inch deep, filled with crystals of sulphate of copper, above which is placed a diaphragm of fearnought, and on the top of this a layer of sawdust, the whole is moistened with water, and a slab of zinc is placed on the top of the sawdust, and has connected to it a wire, a second insulated wire being in connection with the copper tray at the bottom of the cell.

In this case, the oxygen of the water molecule combines with the zinc, forming zinc oxide, and a rearrangement of the molecules takes place throughout the mass, until the copper sulphate is reached; here the liberated hydrogen reduces the copper sulphate, with formation of hydric sulphate and deposition of copper on the copper vessel, whilst the liberated hydric sulphate diffuses through the sawdust and dissolves the zinc oxide on the zinc plate which would otherwise tend to decrease the current; this action again tends to reproduce water, and so the action continues.

In the "Leclanché" cell we have the copper plate replaced by a block of dense carbon—the form used being that obtained from gas retorts, where the heat has caused some of the hydrocarbons present to be decomposed with deposition of carbon, the deposit being especially hard and dense; this carbon plate is surrounded with peroxide of manganese (MnO_2), which is found native as the mineral "Pyrolusite," and this is rendered a better conductor of electricity especially after it has been in use by mixing with it small pieces of carbon. The carbon plate surrounded by the mixture of pyrolusite and carbon is now placed in a porous pot, or bag made of porous material such as canvas or flannel, and this is stood in an outer cell containing a saturated solution of sal ammoniac or ammonic chloride, in which the zinc plate is immersed.

When not in circuit, that is, when there is no connection between the zinc and carbon plate, the zinc is unacted upon, but directly connection is made, the ammonic chloride is decomposed, zinc chloride is formed, ammonia gas and hydrogen are liberated, the hydrogen appearing as before at the carbon plate; here however it meets with the pyrolusite, and combines with some of its oxygen, forming a lower oxide of manganese and water.

This water then dissolves up some more crystals of the ammonic chloride, an excess of which is present, and so the strength of the solution is maintained. The advantages of the Leclanché are, that there is no waste of material when not in use, as the zinc and ammonic chloride do not react until the circuit is closed, and that a solid being employed to absorb the hydrogen, no mixing of liquids takes place.

The peroxide of manganese gives up its oxygen so slowly that when short circuited for a time, it acts almost like a single liquid cell and the carbon is quickly polarised, whilst oxychloride of zinc and a double chloride of zinc and ammonium are formed, which quickly weaken the current.

For intermittent work however, it is one of the best and most lasting of the forms of battery, although not constant.

The current required for firing fuses is considerable, and few batteries of convenient form will give it for any length of time, but for a moment the Leclanché battery is sufficiently powerful, and it will fire the fuses as rapidly as would ever be required in actual practice, and is therefore adopted for firing purposes.

For Service use, the Leclanché is made up in sets of six cells, called "Ship's firing battery," which is used for firing the guns, three-cell boat batteries are used for firing outrigger torpedoes, and ten-cell batteries are used for firing submarine mines and countermines.

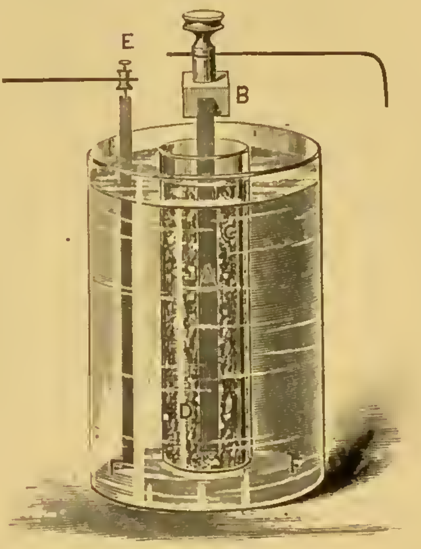

Fig. 16.

In the form of cells used for these purposes, internal resistance is as far as possible reduced by exposing a large surface of zinc and carbon in each cell, and using a partition of fearnought between the carbon and pyrolusite mixture and the ammonic chloride solution containing the zinc.

In the Leclanché cell (Fig. 16) (A) is the carbon plate on to which is cast the lead connection and binding screw (B); (D) is the mixture of pyrolusite and carbon surrounding the carbon plate; and (E) the zinc plate immersed in the saturated ammonic chloride solution (F).

In one form of Leclanché, the carbon and peroxide of manganese are cast into blocks or sticks, and these are fixed to the carbon plate by elastic bands, the whole being kept from contact with the zinc by having a piece of coarse sacking wound round it.

Grove's cell depends upon the solution of zinc in sulphuric acid to generate the current, whilst the negative metal present is platinum, and the liberated hydrogen is oxidised to water by strong nitric acid.

A U-shaped zinc plate (Fig. 17) is immersed in dilute sulphuric acid contained in an ebonite or earthenware vessel, and inside the zinc is placed a porous earthenware pot containing strong nitric acid, in which is the platinum plate.

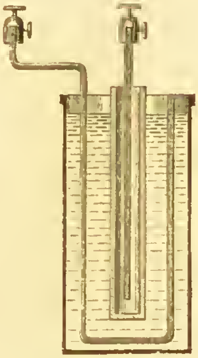

Fig. 17.

The zinc dissolves in the dilute sulphuric acid, forming zinc sulphate and hydrogen; and on the circuit being completed, the usual arrangement of the molecules takes place throughout the liquid, the molecule of hydrogen being liberated on the platinum plate, and in presence of the nitric acid which oxidises it forming water, being itself reduced with evolution of nitrous fumes. The reactions taking place may be represented as—

Zinc + Sulphuric acid = Zinc sulphate + Hydrogen

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

and

Hydrogen + Nitric acid = Water + Nitrous acid.

$$H_2 + HNO_3 = H_2O + HNO_2.$$

The nitrous acid becoming concentrated breaks up into—

Nitrous acid = Nitrogen trioxide + Water

$$2(HNO_2) = N_2O_3 + H_2O.$$

The nitrogen trioxide forms the red fumes escaping after the battery has been some time at work, and is further oxidised by the oxygen of the air into nitrogen tetroxide, which also is a reddish brown gas.

Nitrogen trioxide + Oxygen = Nitrogen tetroxide

$$N_2O_3 + O = 2(NO_2).$$

Some authorities prefer to express the reaction as at once forming the tetroxide.

Nitric acid = Water + Nitrogen tetroxide

$$2(HNO_3) + H_2 = 2(H_2O) + 2NO_2.$$

Nitrous acid has a green colour which can be readily noticed in the acid after use, whilst the gaseous oxides may be seen escaping as red fumes above the battery, and have a highly corrosive action, rendering the use of this form of cell, in a confined space, for any length of time very objectionable. It has a very high electro-motive force and small internal resistance, so that a very strong current can be obtained from it; but, on account of the fumes and the initial expense of the platinum, it is only used when a very powerful current is wanted for a short time.

In "Bunsen's" cell the same construction and liquids are used, but the platinum is replaced by carbon.

The Bichromate battery is a single liquid cell in which zinc is, as before, dissolved in dilute sulphuric acid and the hydrogen generated is oxidised to water by chromic acid, the negative element being formed by carbon plates.

A very ordinary form of this battery is shown at Fig. 18, in which the zinc plate can be drawn up above the surface of the liquid when the cell is not in use, whilst the carbon plates not being acted on, remain stationary.

The cell is charged with potassic bichromate and sulphuric acid, which react upon each other, forming potassic sulphate and chromic acid :—

$$\overset{\text{Potassic bichromate}}{K_2Cr_2O_7} + \overset{\text{Sulphuric acid}}{H_2SO_4} + \overset{\text{Water}}{H_2O} = \overset{\text{Chromic acid}}{2(H_2CrO_4)} + \overset{\text{Potassic sulphate.}}{K_2SO_4}.$$

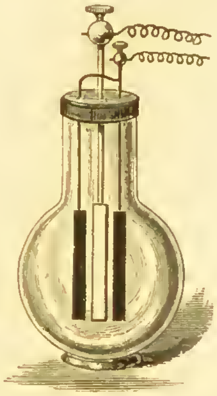

Fig. 18.

On lowering the zinc into the mixture in solution and completing the circuit, hydrogen is evolved, thus :—

$$\overset{\text{Zinc}}{Zn} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Zinc sulphate}}{ZnSO_4} + \overset{\text{Hydrogen}}{H_2}$$

and the hydrogen liberated on the carbon plates is then attacked by the chromic acid which is reduced, and in presence of sulphuric acid forms chromic sulphate and water.

$$\overset{\text{Chromic acid}}{2(H_2CrO_4)} + \overset{\text{Sulphuric acid}}{3(H_2SO_4)} + \overset{\text{Hydrogen}}{3H_2} = \overset{\text{Chromic sulphate}}{Cr_2(SO_4)_3} + \overset{\text{Water}}{8(H_2O)}$$

the chromic sulphate and potassic sulphate so formed crystallising together when the cell is exhausted, as chrome alum. $K_2SO_4Cr_2(SO_4)_3$.

SECONDARY BATTERIES.

When water is decomposed in a voltameter with platinum electrodes, and the battery is taken away and the wires connected with a galvanometer in circuit, the oxygen and hydrogen gradually recombine and a galvanic current will once more flow through the wires, but in an opposite direction to the direct current formed by the battery; and such a source of electricity is called a gas battery.

In the same way if a strong current be passed through slightly acidulated water, between two lead plates, one lead plate becomes oxidised on the surface and coated with a brown powder known as peroxide of lead or lead dioxide (PbO_2); if now the battery be removed and the two electrodes be connected by a wire, a reverse current is produced and one-half the oxygen from the lead dioxide appears on the other lead plate, coating it with litharge or lead monoxide (PbO), so that both plates are now coated with lead monoxide and are alike, and the current ceases.

In practice, the plates are made of cast lead in the form of grids, the holes being about $\frac{1}{4}$-inch square, and one plate has the holes filled with a paste of lead monoxide (PbO) and dilute sulphuric acid, whilst the other has the holes filled with red lead (Pb_3O_4), these plates are then placed in a vessel of dilute sulphuric acid and connected to a dynamo or other generator of electricity and a current passed from the red lead (Pb_3O_4) plate to the lead monoxide (PbO) plate. The lead monoxide is reduced to metallic lead, whilst the red lead is oxidised to lead peroxide

$$\overset{\text{Lead monoxide}}{PbO} + \overset{\text{Hydrogen}}{H_2} = \overset{\text{Lead}}{Pb} + \overset{\text{Water.}}{H_2O}.$$

$$\overset{\text{Red lead}}{Pb_3O_4} + \overset{\text{Oxygen}}{O_2} = \overset{\text{Lead dioxide.}}{3PbO_2}.$$

The plates so prepared being arranged alternately in a vessel are kept apart by indiarubber plugs, the vessel being filled with dilute sulphuric acid (sp. grav. 1.15), and on connecting them a current is set up. Before the action we find lead dioxide (PbO_2) at one plate, and metallic lead at the other, both in presence of sulphuric acid. After action we have lead sulphate ($PbSO_4$) and water (H_2O) formed. Both plates having become coated with lead monoxide (PbO), which has then been converted by the sulphuric acid into lead sulphate ($PbSO_4$).

In all the cells mentioned it is found that the current generated flows from the metal which is acted upon, and which is called the positive metal, through the liquid of the cell to the metal unacted upon and called the negative metal, and then back to the positive metal by the wire connecting the plates outside the cell; and if we break the conducting wire the two ends are called poles, the negative pole being the end connected with the positive metal and the positive pole the one connected with the negative metal of the cell. If these two poles be now dipped into any solution which will conduct electricity, the current (if sufficiently powerful) in passing through the liquid will set up chemical decomposition, a process which is called "Electrolysis." In doing this, the ends of the conducting wires are usually provided with platinum plates, because this metal does not readily enter into combination with the elements or groups of elements liberated on its surface during decomposition. If in this way a current from four Grove's cells be passed through water, acidulated with sulphuric acid to render it a conductor, the water will be decomposed and oxygen will appear at the pole in connection with the platinum of the battery (positive pole) where the current enters the liquid; whilst rather more than double the volume of hydrogen is liberated at the pole in connection with the zinc (the negative pole) where the current leaves the liquid; and if instead of taking water as the substance to be electrolysed (electrolyte), a salt in a fused or dissolved condition be subjected to the action of the current, it is decomposed, and the metal is liberated at the negative pole, and the element or group of elements in combination with it separates at the positive pole; as, however, the compound acid radicles cannot exist in a free condition, and as some of the metals, like sodium and potassium, decompose water when liberated from an aqueous solution of their salts, we find that secondary actions of a chemical nature take place at the poles—for instance, when a solution of salt is electrolysed, chlorine escapes at the positive pole or electrode, whilst for a moment sodium is liberated at the negative pole, but this at once reacts upon the water, forming sodic hydrate and liberating hydrogen, so that the products are sodic hydrate at the negative pole, and free chlorine at the positive. In the electrolysis of potassic sulphate, the potassium is first liberated at the negative pole, but reacting with the water, forms potassic hydrate and liberates hydrogen, whilst the sulphate radicle liberated at the positive pole, first breaks up into sulphur trioxide and oxygen, and the sulphur trioxide dissolving in the water forms sulphuric acid, so that the ultimate products are potassic hydrate and hydrogen at the negative pole, and sulphuric acid and oxygen at the positive.

Potassic sulphate

$$\underbrace{K_2SO_4.}$$

– POLE.			+ POLE.		
Potassium		Water	Sulphate radicle		Water
K_2	+	$2(H_2O)$	SO_4	+	H_2O
Potassic hydrate		Hydrogen.	Sulphuric acid		Oxygen.
$= 2(KHO)$	+	H_2.	$= H_2SO_4$	+	O.

The production of alkaline potassic hydrate and sulphuric acid may be shown by dividing a glass cell into two compartments by means of a vegetable parchment diaphragm (AB) and filling the cell with a strong solution of potassic sulphate coloured with a freshly prepared decoction of red cabbage, which turns green with alkalis and red with acids. On now putting the platinum electrodes (AA) into the solution, one in each compartment, and passing the current from a five-cell Grove's battery, decomposition occurs and the purple solution turns bright red in the compartment containing the positive electrode, and green in contact with the negative (Fig. 16). 19

If, instead of using an aqueous solution of common salt,

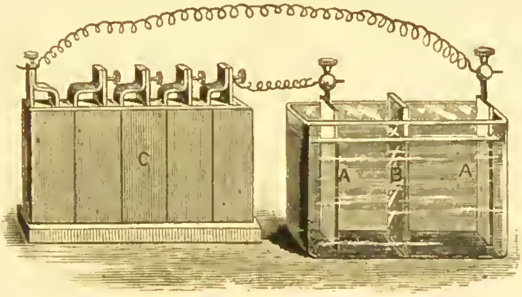

Fig. 19.

the fused salt be taken and carbon plates used as electrodes, then the metal can be liberated and collected, and it was in this way that Sir Humphrey Davy succeeded in isolating sodium and potassium.

When the same galvanic current is made to pass through several metallic solutions contained in separate vessels, it is found that the weights of the metals deposited at the negative poles are in the ratio of their equivalent weights, and that in each cell of the battery as much zinc is dissolved as is equivalent to the metal deposited in each electrolytic cell—for instance, if in each cell of the battery 65 grams of zinc be dissolved, then in the electrolytic cells, 2 grams of hydrogen, 63 of copper, 216 of silver, and so on, will be deposited at the respective negative poles; and if we take chlorides of the various metals, we find that equal volumes of chlorine will be given off at the positive poles, whilst the weight of metal deposited at the negative will vary as its valency, so that if the same current be passed through cupric chloride ($CuCl_2$) and through cuprous chloride (Cu_2Cl_2), if 35.5 grams of chlorine be evolved at each positive pole, 63 of copper will be deposited from the cuprous salt, whilst only 31.5 is thrown out of solution in the case of the cupric salt.

The elements, chiefly non-metals, which appear at the positive pole during electrolysis, are said to be negative elements, whilst those which come off at the negative pole are called positive elements. Formerly great importance was attached to this electrical behaviour, and all elements were arranged in an electro-chemical series in which oxygen figured as the most negative and potassium as the most positive member, and the chemical affinity of the elements was supposed to be governed by their electrical differences, so that when chemical union occurred opposite electricities united. (Electro-chemical theory of Berzelius.) Now, however, less importance is attached to their electrical relations, and it is generally looked upon as established, that the behaviour of the elements in entering into and being expelled from combination, is governed by the thermal changes taking place and in chemical changes the tendency is toward the production of that body or aggregation of bodies, in whose formation there is the greatest development of heat.*

The principles of electrolysis receive a very important application in electro-deposition, which consists in depositing metals from solutions of their salts by a feeble galvanic current —the object on which the metal is to be deposited being made the negative pole, whilst the positive pole consists of a plate of the same metal as that which is being deposited, and this, by its slow solution, keeps up the strength of the liquid.

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* Berthelot. *Méc. Chim.*, 2, 421.

In this way copies may be made of medals, casts, &c.; a mould is first made in fusible metal, plaster, &c., and having been made a conductor of electricity by coating with black lead (graphite), it is connected with the zinc plate of a Daniell's cell, and is immersed in a solution of a salt of the metal to be deposited (generally a cyanide), a plate of the metal is then attached to the copper of the cell and is also immersed in the electrolyte, when the metal is slowly deposited on the mould; in the same way copies may be taken of etchings on metal, and engravings, and metallic substances can be electro-plated.

In order to apply a coating of gold or silver to copper, brass, bronze, or other metallic alloy, the surface should first be very thoroughly cleaned by boiling in a dilute sodic hydrate solution, and the articles are then suspended by a wire in connection with the zinc of some form of feeble battery, in the gilding or silvering bath, whilst a plate of silver or gold as the case may be, is attached to the negative element in the battery, and forms the positive pole in the plating cell.

Messrs. Elkington first introduced the use of cyanides in the solutions to be used for electro-deposition, and the following recipes will give an idea of the solutions in use:

Silver—	Silver cyanide	1 part by weight
	Potassic cyanide	10 ,,
	Water	100 ,,

or—

Silver cyanide	134 ,,
Potassic cyanide	65 ,,

Dilute with water to strength required.

Gold—	Distilled water	1,000 parts
	Sodic phosphate...	60 ,,
	Sodic bisulphite	10 ,,
	Potassic cyanide...	1 ,,
	Gold	1 ,,

The best temperature for electro-plating is about 15° C. or 60° F.

Copper, bronze, brass, or German silver can be electro-plated directly; but steel, zinc and tin must be first coated with a film of copper.

Frequently, the best electro-plated goods have a very thin film of palladium deposited on their surface, in order to prevent the silver being tarnished by sulphuretted hydrogen.

A great interest attaches to the electro-chemical behaviour of metals upon each other when excited by various solutions from the bearing this has upon the condition of the bottoms of ships. Already in the days of wooden vessels this question arose, because copper sheathing was used to protect the timber from fouling, and the attacks of the *Teredo*, a kind of worm which bores its way into wood. The copper acted in preventing fouling by reason of its forming, in contact with the salt water, oxy-chloride of copper, which being poisonous, helped to retard the growth of the germs of certain forms of animal and vegetable life, whilst the wasting of its surface from this cause threw off barnacles and such forms of fouling as obtained hold in spite of the poisonous character of the copper salts. The copper, however, wasted too rapidly; and to prevent this, Faraday advised the use of plates of zinc in metallic contact with the copper, the result being that the zinc and copper excited by the salts in the sea water formed a galvanic couple in which zinc was the positive metal, *i.e.*, the metal dissolved; but this retardation of the destruction of the copper defeated its own purpose, as the copper did not waste or, as it is called, "exfoliate" with sufficient rapidity to throw off barnacles and weed; indeed, the current tended to cause the deposition of earthy matters on the copper surface, which formed a surface well adapted to the growth of marine life.

The same idea was also carried out in Muntz's metal, an alloy of copper and zinc, which, while it had the advantage of being able to be rolled hot into sheets, also caused, when in sea water, less waste of the sheathing, but with the saving of metal the fouling at once increased.

With iron and steel ships the same considerations come into play, and great care has to be taken to prevent the skin of the ship from becoming electro-positive to any other substance: for instance, the bearings of the screw shaft and the valves for the escape of waste water, etc., are made of alloys containing copper; and near these points, where excited by salt water, a strong galvanic action would be set up, attended with rapid destruction of the steel of the shafting, rudder post and plating near these points, because the iron or steel would be electro-positive to the copper alloy and would be therefore the metal acted upon. In order to prevent this, a zinc protector, consisting of a heavy casting of this metal, is placed round all openings where copper or copper alloys are present, and the zinc being more electro-positive than the iron, places the iron in the electro-negative condition, so that whilst the iron is unacted upon, the zinc rapidly dissolves.

Many attempts have been made to cover the bottom of iron ships with zinc plates, to prevent corrosion; but apart from the mechanical difficulties of attachment, it is found that the large surface of metal exposed causes so strong an action that the zinc sheathing wastes too rapidly to make it a practical method.

Many modifications of this idea, such as using very finely-divided zinc as a constituent of protective compositions, have been advocated and tried with results which will be discussed under the heading of protective and antifouling compositions. The consideration of the electro-chemical relations of the metals must also be taken into account in the mooring of vessels, as it is evident that the making fast of an iron or steel vessel to a copper-bottomed ship, or even to another iron vessel, coated with certain compounds of copper in use as antifouling compositions, would be sufficient, if the connection were made by a steel hawser or even a wet rope, to set up galvanic action at the expense of the iron ship. For the same reason copper-bottomed vessels should not be made fast to iron piers, or iron or steel ships to piers protected by copper.

CHAPTER IV.

OXYGEN.

Occurrence—Preparation of oxygen gas—Oxygen obtained from air—Properties of oxygen—Combustion in oxygen—Oxides—Acid forming oxides — Bases — Salts — Combustion — Slow combustion — Respiration—Spontaneous combustion—Combustion by combined oxygen—Ozone.

OXYGEN the second constituent of water, is the most abundant of the elements, and is not only found in air and water, but also constitutes nearly 45 per cent. of the solid crust of the globe.

The fact that a film forms on the surface of many metals when heated and exposed to air, was known from the earliest times, and in 1774, Priestly working with mercuric oxide—the film so formed on mercury—found that it could be decomposed at a high temperature into mercury and oxygen, which was thus first prepared and examined, and a little later Lavoisier showed the part it plays in combustion and gave it the name it now bears. It may be prepared—

1. By heating mercuric oxide, which breaks up into mercury and oxygen.

$$\underset{\text{Mercuric oxide}}{2(HgO)} = \underset{\text{Mercury}}{2Hg} + \underset{\text{Oxygen.}}{O_2}.$$

2. By heating "Pyrolusite" (peroxide of manganese) in an iron vessel to a high temperature, when it gives off ⅓rd of its oxygen and forms a lower oxide.

$$\underset{\text{Peroxide of manganese}}{3(MnO_2)} = \underset{\text{Trimanganic tetroxide}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}.$$

Some oxides, like mercuric oxide, give off the whole of their oxygen on heating; others, of which the peroxide of manganese or manganic dioxide may be taken as a type, only give off a portion, whilst the members of a third class like potassic or sodic oxide are not broken up by heat.

3. By passing steam and chlorine through a hot porcelain tube, when the hydrogen and chlorine unite to form hydrochloric acid and oxygen is liberated. On collecting the gases over water the hydrochloric acid is absorbed and only pure oxygen is left. (See p. 10.)

$$\overset{\text{Steam}}{2(H_2O)} + \overset{\text{Chlorine}}{2Cl_2} = \overset{\text{Hydrochloric acid}}{4(HCl)} + \overset{\text{Oxygen.}}{O_2.}$$

4. By heating potassic chlorate, a compound of potassium, chlorine and oxygen, when oxygen is liberated and potassic chloride left. This decomposition takes place in two stages, oxygen, potassic chloride and perchlorate being formed, and then the perchlorate so produced rapidly breaks up into potassic chloride and oxygen.

$$a. \quad \overset{\text{Potassic chlorate}}{2(KClO_3)} = \overset{\text{Potassic perchlorate}}{KClO_4} + \overset{\text{Potassic chloride}}{KCl} + \overset{\text{Oxygen.}}{O_2.}$$

$$b. \quad \overset{\text{Potassic perchlorate}}{KClO_4} = \overset{\text{Potassic chloride}}{KCl} + \overset{\text{Oxygen.}}{2O_2.}$$

This is the usual method adopted for its preparation.

The decomposition may be effected much more rapidly by mixing a little peroxide of manganese with the potassic chlorate, which effects the breaking up of the chlorate ~~to proceed~~ at a much lower temperature and more rapidly. If the temperature rises much above 300° the gas comes off with great violence, and is often found to contain small traces of chlorine, liberated by the decomposition of some of the potassic chloride.

The relative rates at which the gas is evolved from the chlorate alone, and from chlorate mixed with the manganic peroxide, may be shown by performing the operations side by side (Fig. 20) and collecting the gas formed in two cylinders of equal size (AA). The chlorate is heated in the retort (B) fitted with a delivery tube leading under water in the pneumatic trough, whilst the mixture of chlorate and manganic dioxide is heated in the Florence flask (C), and the gas, before collecting, is washed by passing through water in the two-necked bottle (D).

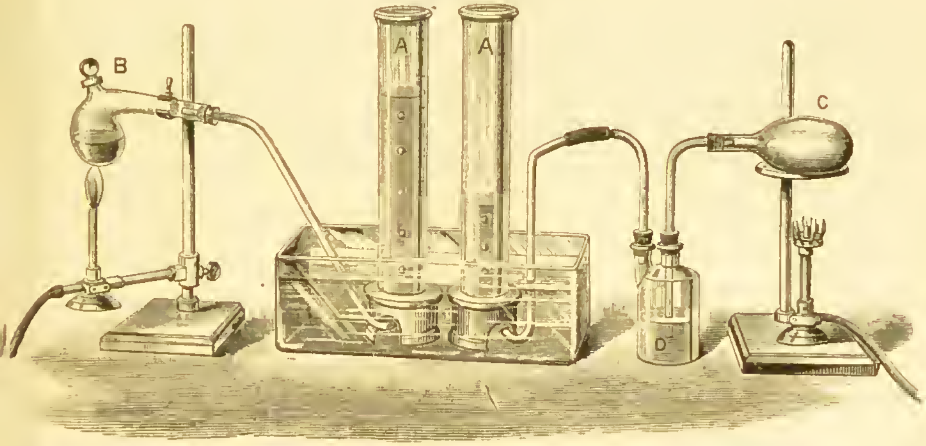

Fig. 20.

Oxygen existing free in the atmosphere, one might expect that air would be the cheapest and best source from which to obtain it; but this is not so, as nitrogen, with which the oxygen in air is diluted, has such feeble affinities for other substances that it is impossible to absorb it so as to leave the oxygen pure, whilst if oxygen be extracted by chemical means it forms such strong compounds that it cannot easily again be liberated from them.

As we have already seen, it can be made to combine with mercury and the oxygen can then be recovered from the mercuric oxide, but this is a tedious and costly process. The best method yet devised for extracting oxygen from air is by heating baric oxide in a current of air; the baric oxide takes up another atom of oxygen becoming baric dioxide, and this if heated to a higher temperature than that at which it was formed, gives off its acquired oxygen, becoming baric oxide once more.

$$\underset{\text{Baric peroxide}}{2(BaO_2)} = \underset{\text{Baric oxide}}{2(BaO)} + \underset{\text{Oxygen.}}{O_2}.$$

It is upon this reaction that the process of Brin Frères, for the production of oxygen on a large scale, is based.

Anhydrous barium oxide is placed in a series of retorts heated to 500° to 600° C., whilst air carefully freed from carbon dioxide is passed through them; the oxygen being absorbed by the baric oxide produces baric peroxide, the flow of air is then stopped and the temperature raised to 800° C., when decomposition takes place, pure oxygen being evolved.

M.M. Brin calculate that one kilo. of their baric oxide will produce nearly fifty liters of oxygen at each operation.

Another process for obtaining oxygen from air depends upon the fact that the oxides of manganese when heated in contact with alkalis and air are able to absorb oxygen from the air and will give it off again when heated in a current of steam.

There are other methods for preparing the gas, but they are of scientific rather than general interest.

Oxygen is a colourless, odourless, tasteless gas; it is 16 times heavier than hydrogen, hence we say its density is 16, and it is only slightly soluble in water—at ordinary temperatures 100 volumes of water dissolve 3 volumes of the gas, but the amount so dissolved depends to a great extent upon the temperature; at 0° C. 100 vols. water dissolve 4 vols. of gas, whilst at 20° C. they dissolve only 2.8 volumes. Small as this amount is, it plays a most important part in Nature, as it is required for the support of fish life and also tends to destroy any refuse organic matter which may find its way into the water.

Oxygen can only be condensed to the liquid state by a combination of intense cold and enormous pressure, a temperature of – 140° C. and a pressure of 320 atmospheres, being required for its liquefaction. The gas has no action upon test papers and does not turn lime water milky.

All bodies which burn in the air burn with increased brilliancy in oxygen gas, and many substances which do not ordinarily burn in air, such as iron, can be made to do so in oxygen.

If we burn sulphur, phosphorus, or carbon, in oxygen, we obtain oxides which on solution in water form acids, and these acid forming oxides are sometimes called anhydrides.

Sulphur — Oxygen — Sulphur dioxide or Sulphurous anhydride.

$$S + O_2 = SO_2.$$

Phosphorus — Oxygen — Phosphoric pentoxide or anhydridc.

$$4P + 5O_2 = 2(P_2O_5).$$

Carbon — Oxygen — Carbon dioxide or anhydride.

$$C + O_2 = CO_2.$$

And these combined with water yield the corresponding acids:

Sulphur dioxide — Water — Sulphurous acid.

$$SO_2 + H_2O = H_2SO_3.$$

Phosphoric pentoxide — Water — Phosphoric acid.

$$P_2O_5 + 3H_2O = 2(H_3PO_4).$$

Carbon dioxide — Water — Carbonic acid.

$$CO_2 + H_2O = H_2CO_3.$$

These substances have a strongly acrid taste, and when brought in contact with a blue vegetable colouring matter called litmus turn it red. Lavoisier having observed this fact supposed that all bodies burnt in oxygen would yield acids as the product of their combustion, hence he gave it the name of oxygen, from the Greek *oxus* (acid) and *gennao* (I produce). If we carefully examine the products of the combustion of various elements in oxygen, we find that it is only the non-metallic which on combustion yield these strongly acid oxides. If we take the product formed by the combustion of iron in oxygen, it has no acid taste or action on litmus; again, if we burn sodium in oxygen, not only is there no acid formed, but the product of combustion has properties diametrically opposed to those of an acid, and when dissolved in water the solution has a soapy taste and turns to blue the litmus originally reddened by the acid. All the elements, with the exception of fluorine, combine with oxygen.

Oxygen acts very differently on the different metals; some metals, such as zinc, magnesium, and calcium, take fire when heated and burn with evolution of light, whilst others, such as gold and silver, do not combine directly with it, and can only be converted into oxides by indirect means.

The compounds of oxygen with the elements may be divided into three classes:—

1. Acid forming oxides or anhydrides, which are usually the oxides of the non-metals and some higher oxides of the metals.
2. Basic oxides, which are oxides of the metals.
3. Indifferent or neutral oxides, which are some oxides of the non-metals and peroxides of the metals.

As types of the first class may be taken—

Sulphur dioxide (SO_2).
Carbon dioxide (CO_2).
Chromic trioxide (CrO_3).
Silica (SiO_2).

In the second class—

Cupric oxide (CuO).
Ferric oxide (Fe_2O_3).
Calcic oxide (CaO).
Sodic oxide (Na_2O).

In the third class—

Hydrogen monoxide (H_2O).
Nitrogen dioxide (NO).
Lead peroxide (PbO_2).
Baric peroxide (BaO_2).

The normal oxides of the metals are called bases, and when soluble are alkaline in their properties. When a soluble basic oxide is brought in contact with water it chemically combines with it, forming a body called a hydrate.

Calcic oxide		Water		Calcic hydrate.
CaO	+	H_2O	=	$Ca(HO)_2$.
Sodic oxide				Sodic hydrate.
Na_2O	+	H_2O	=	$2(NaHO)$.
Potassic oxide				Potassic hydrate.
K_2O	+	H_2O	=	$2(KHO)$.

When an acid is brought in contact with a basic oxide or a metallic hydrate, the metal of the base replaces the hydrogen, and we obtain a compound called a salt, water being at the same time eliminated.

BASE		ACID		SALT		WATER.
Sodic oxide		Carbonic acid		Sodic carbonate.		
Na_2O	+	H_2CO_3	=	Na_2CO_3	+	H_2O.
Calcic oxide		Sulphurous acid		Calcic sulphite.		
CaO	+	H_2SO_3	=	$CaSO_3$	+	H_2O.
Sodic hydrate		Carbonic acid		Sodic carbonate.		
$2(NaHO)$	+	H_2CO_3	=	Na_2CO_3	+	$2(H_2O)$.
Calcic hydrate		Sulphurous acid		Calcic sulphite.		
CaH_2O_2	+	H_2SO_3	=	$CaSO_3$	+	$2(H_2O)$.

When free, oxygen can be detected—

(*a*) By its power of supporting combustion.
(*b*) By its forming a reddish brown gas when brought in contact with the colourless gas nitric oxide.
(*c*) By its being absorbed by potassic pyrogallate with formation of a deep brown compound.

Oxygen being the constituent of our atmosphere which supports life and combustion, it is commonly considered as *the* supporter of combustion, whilst those bodies which will combine with oxygen with evolution of heat and light are called combustibles. Combustion, however, is merely chemical combination of a very energetic description; and the terms "combustible" and "supporter of combustion" are purely relative, as under altered conditions the combustible may become a supporter of combustion. For instance, coal gas burns in air, hence we say that coal gas is a combustible and air the supporter of combustion, but we find that in an atmosphere of coal gas we can burn air, showing that under these altered conditions air has become the combustible and coal gas the supporter of combustion.

Ordinary combustion therefore is the evolution of heat and light during rapid and energetic chemical action; but in Nature there are many cases of chemical changes which are so gradual that the heat evolved, being spread over a long period of time, becomes inappreciable to our senses, and such processes we call slow combustion.

A tree left to rot upon the ground gradually disappears in the course of years, being oxidised up into carbon dioxide and water vapour and scarcely any evolution of heat is observed, yet the same amount of heat is generated as if the tree had been cut into logs and burnt.

When a steel watch-spring is kindled in oxygen gas by means of a piece of German tinder attached to the end of it, the iron burns away with great rapidity, forming an oxide of iron and giving out great heat and also light. The same weight of metal would in the course of time, if exposed to moist air, be converted into an oxide which, combined with water, is ordinary iron rust; yet no evolution of heat is perceptible, because the time over which the action is spread is so great, that at no one moment of time is enough heat evolved to be perceived by our senses; yet in each case the total quantity of heat evolved is the same. Another example of slow combustion is found in the act of respiration.

In order to fully understand this we must consider what takes place during the respiration of animals. The blood is distributed to the body by a complete set of pipes, one set carries blood from the heart and are called arteries, whilst another set carries blood to the heart, and these are called veins; between the extremities of the arteries and the commencement of the veins, we find a minute system of vessels called the "capillaries," which connect the arteries and the veins. The heart is divided into four chambers, and the blood brought to the heart by two great veins, one from the lower and the other from the upper extremities, these empty themselves into the right upper chamber; from this it passes into the right-hand lower chamber, whence it passes through a vessel which terminates in the capillaries of the lungs. These capillaries communicate with four large veins which bring the blood back to the left-hand upper chamber of the heart, whence it passes into the left-hand lower chamber and is forced out into the great artery, which distributes it to the different organs and tissues of the body. In the lungs the blood comes in contact with the inspired air, admitted to the air cells of the lungs by the windpipe, and here a great change takes place in the character of the blood; the blood as it comes into the lungs is purple, and is charged with carbon dioxide, but in the air cells of the lungs this gas passes out from the blood and oxygen passes in, by a process called diffusion, and takes its place, whilst the colour of the blood turns from purple to red and passes back through the heart to the artery and the system; here in the capillaries the tissues of the body take the oxygen from the blood, replacing it by carbon dioxide, with the result that it again changes to purple, and in this condition returns by the veins to the heart and lungs, once more to give up carbon dioxide and take in a fresh supply of oxygen. The purple blood is called "venous" or the blood of the veins; the bright scarlet blood is called "arterial."

Whenever we move some of the tissues of the body are used up, and this waste matter unless removed would accumulate and cause death. The tissues consist chiefly of carbon, nitrogen and hydrogen; and when the oxygenated blood meets these it attacks and burns them, converting the hydrogen into water which escapes as perspiration, exhaled moisture, and urine, whilst the carbonic acid is brought back to the lungs and discharged with the expired air, and it is this process of slow combustion which maintains the heat of our bodies. Slow combustion, due to oxidation, is in some cases followed by rapid combustion, for instance, many oils will undergo an oxidising action in air, being converted into resinous bodies, and if this takes place under conditions where the heat generated cannot escape, the temperature gradually rises until a point is reached when slow combustion becomes rapid combustion, and the mass bursts into flame. A heap of greasy or oily rags left exposed to air gradually "heats," and the cotton waste or cotton rags being bad conductors of heat, many cases of spontaneous combustion can be traced to this cause. Exactly the same combination of oxidation and insulation of the heat generated gives rise to the spontaneous firing of haystacks when the hay has been stacked before it was properly dry.

Most kinds of coal contain a sulphide of iron called "pyrites," and this in contact with moist air gradually undergoes oxidation with generation of heat. In small quantities of coal the temperature is kept down by free access of air; but where coal is stored in large quantities, as in the coal bunkers of a ship, the heat generated in the middle of the mass cannot escape, the temperature rises, inflammable gases re generated from the coal, and in some cases explosion or pontaneous firing of the coal results.

The influence which the rapidity of oxidation has upon emperature may be shown by taking a hard glass tube conaining some finely-divided oxide of iron, passing a slow urrent of dried hydrogen gas over it, and at the same time eating it. The hydrogen reduces the oxide, forming water, hich escapes as steam, whilst the iron is left in the form of very finely divided powder, which is allowed to cool in the tream of hydrogen gas; the tube is then sealed up whilst still ull of gas, care being taken to admit no air. On opening uch a tube (called a pyrophorus) and shaking out the finely-ivided metal into the air, it is at once oxidised and the heat enerated is sufficient to make it red hot, the fine state of ivision affording a very large surface for the oxygen of the ir to act upon. If now the same weight of iron be taken in compact form, such as wire, it would take several months, f not years, for air and moisture to convert it into oxide, and he heat generated is spread over so long a period of time that e do not perceive its evolution; but even in this case, if urrounded with a nonconductor, a temperature might e reached which would be perceptible. A case of this kind ccurred during the manufacture of the Mediterranean teleraph cable, which was enclosed in a strong casing of iron wire nd tightly coiled in water tanks, 163 miles of it being wound n a coil 30 feet in diameter. The tank in which this was conained leaked and the water ran off, leaving the wire casing of he cable exposed to air, and the moist metal oxidised so apidly that sufficient heat was generated to form considerable uantities of vapour and to give rise to serious fears as to the oftening of the indiarubber covering of the core and damage o the insulation.

Oxygen is, under some circumstances, induced to combine ith another substance by the influence exerted by the surface of a third, which takes no apparent part in the chemical action. If we take a piece of platinum foil, and having heated it, allow it to cool down somewhat, and then expose it to a stream of hydrogen and air, the platinum again becomes red-hot and may be kept glowing in the stream of mixed gases for any length of time. Platinum has the power of attracting to its surface both hydrogen and oxygen; and under these conditions the gases being in an increased condition of activity, combine, and by the heat of their combination make the platinum red hot. If platinum in the condition of fine powder (platinum black) be employed, the action is even more energetic, the mixed gases being inflamed.

In very many cases oxidation can be effected by "combined oxygen," that is to say, certain compounds which contain large quantities of oxygen are capable of giving it up to readily oxidisable substances with which they are brought in contact, the conditions being such that chemical action can take place. For instance, potassic chlorate, as we have seen, holds large quantities of oxygen in such loose combination that merely heating it above the temperature at which it fuses is sufficient to drive it off. If now we throw any oxidisable substance upon the surface of fused potassic chlorate, we find that it burns with great vigour at the expense of the oxygen of the chlorate.

Again, potassic permanganate, a body rich in oxygen when mixed with strong sulphuric acid, has the power of giving oxygen to all substances which can take it up, and will even oxidise substances which do not combine with oxygen under ordinary conditions.

This property is of enormous importance to us in the manufacture of explosives, as it enables us in a small space to supply combustible bodies with others which are capable of supplying sufficient oxygen for their combustion. In gunpowder the charcoal and sulphur are readily combustible, whilst he saltpetre or potassic nitrate is the storehouse of oxygen which supports their combustion, with generation of great heat.

OZONE.

At the close of the last century, Van Marum observed a peculiar odour whilst working his great electrical machine at Haarlem; and in 1840 the Swiss chemist, Schönbein, showed that when electric sparks are passed through oxygen, or buildings are struck by lightning, the same odour is observed; and it has been shown that the odour is due to a modification of oxygen, to which, on account of its odour, the name of ozone has been given. If ozone be experimented upon it is found to be identical in chemical composition with oxygen, but physically it is very different, being also much more active in its oxidising properties and corroding substances upon which oxygen has no effect.

When elements change their physical properties and activity and yet remain unaltered in composition they are said to be "allotropes," or allotropic modifications, and this allotropism is due to a rearrangment of the particles of which the mass is built up. Thus ozone is said to be an allotropic modification of oxygen. The analogous change of properties in compounds is called "isomerism;" for instance, chalk and Iceland spar are both of them calcic carbonate and are chemically the same, although they differ widely in properties: hence they are said to be "isomeric."

Oxygen may be made to assume the condition of ozone in several ways—

1. By the passage of silent electric discharges, as when oxygen passes between surfaces charged with opposite electricities.

This may be effected in the apparatus shown in Fig. 21. A slow stream of oxygen is passed through the cylinder (A) from a reservoir of the gas, and a little water at the bottom of the cylinder allows the rate at which it is passing to be seen. The gas then passes on through the ozonising tube (B), in the centre of which is a tube filled with mercury and connected with one pole of the coil (D), the other pole being in connection with water in the cylinder (C) which surrounds the ozonising tube. In this way the oxygen is made to pass through a contracted space, through which a brush discharge is passing from the mercury to the water, with the result that some of the oxygen is converted into ozone and may be collected by downward displacement.

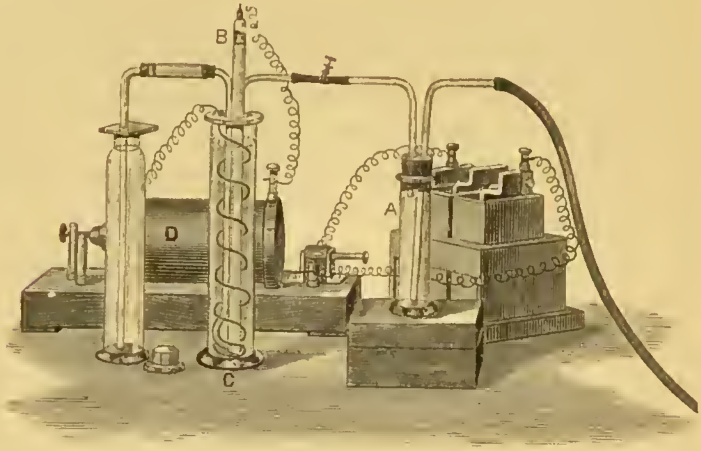

Fig. 21.

2. Ozone is formed in contact with substances undergoing slow oxidation in presence of moisture.

This is shown by half covering a freshly scraped stick of phosphorus with water, in the bottom of a large flask, the mouth of which is closed by a glass plate. The phosphorus slowly oxidises at the expense of some of the oxygen of the air, the products dissolving in the water, whilst a considerable amount of ozone is at the same time formed and may be detected by the usual tests.

3. When water is decomposed by electrolysis, a certain proportion of the oxygen liberated at the positive pole is converted into ozone.

Ozone may be recognised by its smell, which is sometimes erceived at sea or in the open country, and which can be etected when there is only 1 volume of ozone present in 2½ illion volumes of air. It can also be detected by its action upon mixture of starch and potassic iodide, which is generally used pread upon paper. Ozone has so strong an oxidising action hat it breaks up potassic iodide, oxidises the potassium to otassic oxide and liberates iodide, which immediately combines with the starch, forming a deep blue coloured compound. ther bodies besides ozone possess this same power, so that it is ell to supplement this test by a second, which consists of red tmus paper dipped in a dilute solution of potassic iodide. In ontact with ozone the decomposition of the iodide and beration of potassic oxide takes place as before, and potassic xide being a strong alkali, turns the red litmus to blue. This esult, taken in conjunction with the other, affords a sure test r ozone.

Ozone will exercise a bleaching action on dilute solutions f indigo, and attacks vulcanised caoutchouc with great apidity; brought in contact with metallic mercury it soon arnishes the surface owing to formation of oxide. It is entirely bsorbed by oil of turpentine, and at a temperature of 149° C. zone is at once reconverted to ordinary oxygen.

When oxygen is converted into ozone, at most one fifth of he volume present, generally far less, is ozonised, and the rmation of ozone is attended with a contraction of volume. We have seen that the density of oxygen on the hydrogen cale is 16, and if we take 12 volumes of oxygen and pass the rush discharge until contraction ceases, we find we have 11 volumes of mixed ozone and oxygen left; on introducing ome turpentine into this mixture all the ozone is absorbed, and 9 vols. of oxygen are left, so that 2 vols. of ozone were present and had been produced by 3 vols. of oxygen. Let the 12 vols. of oxygen weigh $12 \times 16 = 192$, then the 9 vols. left will $= 16 \times 9 = 144$, $192 - 144 = 48$, the weight of the 2 vols. of ozone formed, and therefore 1 vol. of ozone $= 24$, or one third heavier than an equal vol. of oxygen.

It has been shown that the molecule of oxygen contains two atoms and is represented by O_2, and it follows, therefore from the above experiment that ozone must contain 3 atoms in the molecule and will be represented as O_3, its great tendency to act as an oxidising agent being due to the loose hold it has on the third atom of oxygen which is readily given up to any oxidisable substance. This view of its action is corroborated by the fact that when ozone oxidises a substance no alteration in volume of the gas takes place.

$$\underset{\text{Mercury}}{Hg} + \underset{\text{2 vols. ozone}}{O_3} = \underset{\text{Mercuric oxide}}{HgO} + \underset{\text{2 vols. oxygen.}}{O_2}.$$

Although ozone in small quantities is one of the strongest agents in Nature for the destruction and removal of waste organic matter, yet when present in larger quantities it is a violent poison, acting as an intense irritant to the eyes and nose, and rapidly proving fatal.

Ozone decomposes slowly in presence of moisture at temperatures above 100° C., and is completely broken up with great rapidity at temperatures above 230° C. *

The facts that oxygen can be converted into ozone by the brush discharge, and the ozone so formed reconverted into oxygen by the action of heat, prove conclusively that ozone and oxygen are merely allotropic modifications of the same element.

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* Andrews and Tait.

CHAPTER V.

COMPOUNDS OF HYDROGEN WITH OXYGEN.

Water—Composition of water by volume and weight—The formula or water—Physical properties of water—Latent heat—Specific heat—Change of volume during change of state—Boiling point of water—Spheroidal state—Solution—Water of crystallisation—Water of hydration—Circulation of water in Nature—Natural waters—Hydric dioxide.

A LITTLE more than one hundred years ago Cavendish showed, that when oxygen and hydrogen were mixed together in the proportions of two vols. of hydrogen to one of oxygen and the mixture exploded, water and nothing but water, was formed. Since that time the composition of water has been investigated by many chemists, whose results confirm the experimental facts arrived at by Cavendish, and explained by Lavoisier during the years 1781-83.

Whenever hydrogen or any substance containing hydrogen, such as coal, wood, fat, &c., burns in air or oxygen, water is produced, and it has been shown (p. 10) that by the decomposition of water the gases, oxygen and hydrogen, can once more be obtained. We have also seen that the ratio in which these gases combine by volume, is two volumes of hydrogen to one of oxygen, this being conclusively proved by the eudiometric synthesis of water. Knowing that the atoms of oxygen are 16 times heavier than the atoms of hydrogen, it would be easy to deduce the proportions by weight, in which the two elements combine, and this can be also experimentally determined by passing hydrogen gas generated from zinc and dilute sulphuric acid in the generating bottle (A, Fig. 22), through the tube (B), which is filled with anhydrous calcic chloride, and which will absorb any moisture the gas may contain. The dried hydrogen now passes over heated oxide of copper in the tube (C) and reduces it to metallic copper, combining with the oxygen and forming steam which passes on and condenses in the U tube (D), which is kept cool by standing in a vessel of water, whilst any moisture which escapes condensation is taken up by the chloride of calcium tube (E).

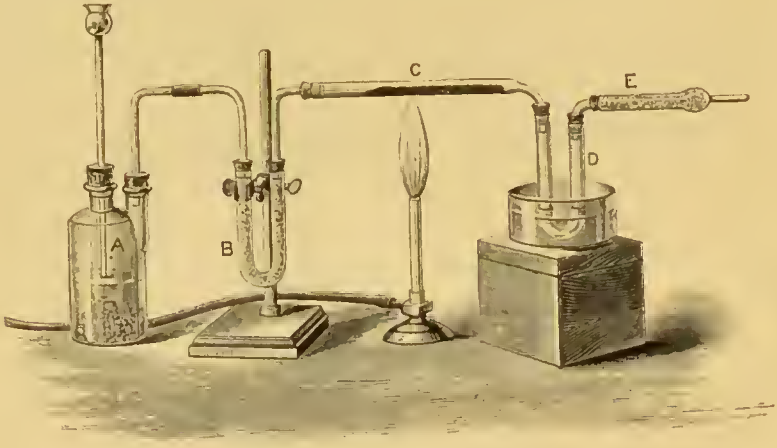

Fig. 22.

$$\overset{\text{Hydrogen}}{H_2} + \overset{\text{Cupric oxide}}{CuO} = \overset{\text{Copper}}{Cu} + \overset{\text{Water.}}{H_2O.}$$

If the tube containing the copper oxide be weighed before the experiment, and again after the experiment is finished, the loss of weight will represent the oxygen taken up by the hydrogen to form water, whilst the increase of weight in the vessels arranged to condense the steam will give the weight of water formed. For instance, suppose the tube containing the copper oxide, before the experiment, weighs 179.5 grams, and after the experiment only 163.5 grams, the loss in weight representing oxygen used up by the hydrogen to form water is 16 grams; and if we weigh our condensing tubes we find we have collected 18 grams of water—therefore, this 18 grams of water must consist of 16 grams of oxygen combined with 2 grams of hydrogen; or, in other words, $\frac{1}{9}$th of the weight of water is due to hydrogen and $\frac{8}{9}$ths to oxygen.

We determine the formula of a compound by analysing it and expressing its composition in parts per 100, so that our analysis of water would give us the percentage composition.

$$\begin{array}{lr} \text{Hydrogen} \ \ldots \ \ldots & 11.1\dot{1} \\ \text{Oxygen} \ldots \ \ldots & 88.8\dot{8} \\ \hline & 99{\cdot}9\dot{9} \end{array}$$

Now divide each of the percentages so obtained by the atomic weight of the constituent to which it refers, and the numbers so obtained will have the same ratio as the number of atoms present in the compound.

$$\frac{11{\cdot}11 \text{ (percentage of H)}}{1 \text{ (atomic weight of H)}} = 11{\cdot}11 \qquad \frac{88{\cdot}88 \text{ (percentage of O)}}{16 \text{ (atomic weight of O)}} = 5{\cdot}5$$

and 11·11 stands to 5·5 as 2 to 1.

The formula for water is therefore H_2O, or some multiple of H_2O, such H_4O_2, &c. This is called the empirical formula, and merely shows the ratio of atoms in the molecule. When water is acted upon by sodium or potassium the hydrogen can be replaced in two successive stages, forming the hydrates, and the oxides :—

$$\begin{array}{ccccccc} \text{Potassium} & & \text{Water} & & \text{Potassic hydrate} & & \text{Hydrogen.} \\ K_2 & + & 2(H_2O) & = & 2(KHO) & + & H_2, \end{array}$$

and by acting on fused potassic hydrate with potassium, the remainder of the hydrogen is expelled.

$$\begin{array}{ccccccc} \text{Potassic hydrate} & & \text{Potassium} & & \text{Potassic oxide} & & \text{Hydrogen.} \\ 2(KHO) & + & K_2 & = & 2(K_2O) & + & H_2\,; \end{array}$$

showing that the molecule of water contains two atoms of hydrogen and that its formula must therefore be H_2O, and this gives us the true molecular formula.

Water exists in Nature in three forms: as ice, water and steam. Below 0° C. it exists as ice, from 0° to 100° C. as water, and above that temperature as steam.

If we take a vessel containing ice and place a thermometer in it, the mercury falls to 0° C.; if now a flame be placed under the vessel, no rise of temperature is observed until every particle of ice is melted.

The heat so used up in melting the ice is said to be rendered latent; and it has been found by experiment that in passing from the solid to the liquid state a given weight of ice renders latent as much heat as would raise the same weight of water from 0° C. to 79° C. The latent heat of water is therefore said to be 79 thermal units—a thermal unit meaning the quantity of heat required to raise a unit weight of water one degree Centigrade. When water freezes, this amount of heat is again given out.

Heat is absorbed when a solid becomes a liquid or a liquid becomes a gas, and the heat is again developed as sensible heat when the reverse changes take place; and it is upon this principle that nearly all freezing mixtures and other devices for lowering the temperature are devised.

Nearly all bodies contract when cooled and expand when heated, but between certain temperatures water is an exception to this rule. If we take water at its boiling point and gradually cool it, we find it contracts with regularity until it reaches a temperature of 4° C., at this point it begins to expand, and continues to do so until at 0° C. it is converted into ice, when a sudden and still greater expansion takes place. Hence we say that the point of maximum density of water is 4° C., because a given bulk of water will weigh more at this temperature than at any other. Although the amount of expansion, from 4° C. to 0° C., is very small, yet it exerts an mmense influence upon our climate. When water expands t becomes lighter: hence the water cooler than 4° C. always emains on the surface of a pond or lake, and the surface reezing first protects the water below it from the cold. If ater continued to contract on cooling, all water would be onverted into solid masses of ice, which would not ntirely melt in the hottest summer—a state of things which ould not only destroy all fish, but would render our climate lmost arctic in its nature.

When water is heated to 100° C. under normal barometric onditions, it commences to boil, and as long as the steam enerated is allowed to freely escape, no further rise in temerature takes place, the whole of the additional heat being endered latent in converting the liquid into a gas.

The latent heat of steam is said to be 536 thermal units, ecause if we take 100 grams of water at 0° C. and pass steam nto it, 18.6 grams of steam will be condensed before the mass s heated to 100° C. Now, 18.6 is to 100 as 1 to 5.36, so that unit weight of steam in condensing, gives out enough heat o raise 5.36 units of water from 0° C. to 100° C., or 536 unit eights of water from 0° C. to 1° C.

Water has a greater capacity for heat than any other ubstance, and therefore requires more heat to raise it to any iven temperature than an equal weight of any other subtance. This property has a great influence upon climate, as he countries which are surrounded with water have a ore equable range of temperature than those from which ater in bulk is absent.

During the summer months the excess of heat is absorbed y the water without its becoming unduly heated, whilst in e winter this heat is again given out and prevents too udden changes in temperature.

Water boils when the tension of its vapour is equal to the uperincumbent atmospheric pressure; therefore at the top of a mountain, where the atmospheric pressure is less than at the sea level, water boils below 100° C., but at the bottom of a deep mine, where the pressure of the atmosphere is greater, water has to be heated above 100° C. before it is converted into steam. This may be shown by warming water to about 80° to 90° C. in a flask (A, Fig. 23) and attaching it to an air pump; an empty bottle (B) and a long tube filled with calcic chloride (C) being interposed in order to condense and absorb water vapour and so prevent any reaching the air pump. On giving a few strokes of the air pump, the pressure is reduced on the surface of the water in the flask and the water boils briskly. This principle is applied in the sugar maker's vacuum pan, in which water is boiled off from the saccharine syrup at temperatures far below the boiling point in air; and also in "Papin's digestors," where, by increasing the pressure, the boiling point is raised.

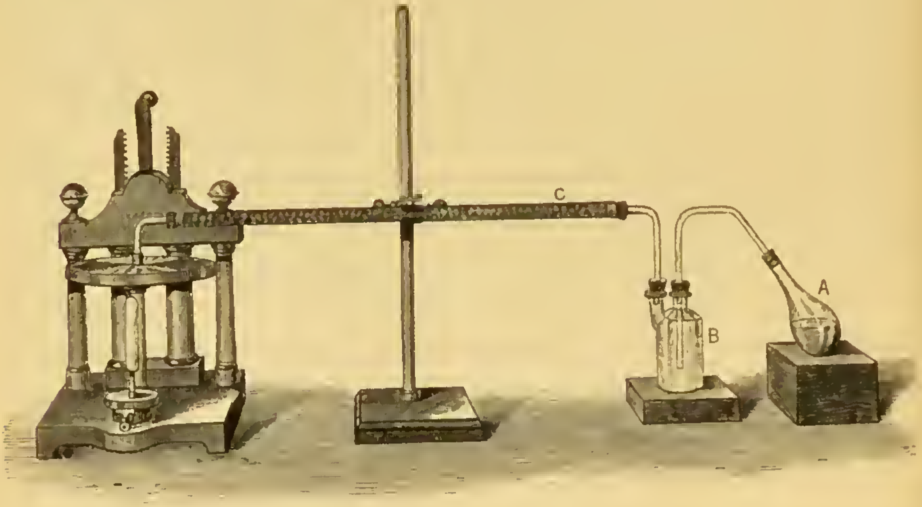

Fig. 23.

Although water does not boil under ordinary conditions of atmospheric pressure until the tension of its vapour is equal to the pressure of the atmosphere upon its surface, yet we find that even at temperatures below the freezing point it slowly evaporates, as is shown by the gradual evaporation of water left exposed to air in a saucer, and even by the gradual disappearance of snow. This used to be explained as being due to the air having the power of dissolving water; but it can be shown that air has nothing to do with it, as water will evaporate just as well into a vacuum, the property being due to the elastic force of the vapour.

When water is thrown upon a heated silver dish it is seen to assume a spheroidal form and does not boil, although the plate or dish is heated very far above its ordinary boiling point. If the dish be now allowed to cool, at a certain point the water suddenly bursts into violent ebullition and is converted into steam. This spheroidal form is due to the generation of a cushion of steam between the water and the heated surface which prevents the water coming in contact with it, so that it only slowly evaporates away; but on allowing the temperature to fall, a point is reached when the heat is no longer sufficient to rapidly generate the steam which supports the water like a cushion, the water comes in contact with the hot plate and in a moment is converted into steam.

This has been shown by Perkins to hold good in the case of boilers, so that if a boiler has been allowed to run dry and the plates have been highly heated, on the entrance of feed-water the first portions assume the spheroidal state, but as more water is added and the plates are gradually cooled, contact takes place with formation of enough steam, in many cases, to cause explosion.

In masses pure water has a blue colour, but a very small percentage of impurities imparts to it a greenish tint. Water is practically incompressible, a pressure of 30,000 lb. only compressing 14 volumes into 13. The weight of water at 4° C. is taken as the unit of comparison for solids and liquids, so that when iron is said to have a specific gravityof 7.8, it means that a given bulk of water is taken as weighing 1 at

4° C., and that the same bulk of iron would weigh 7.8. One gallon of water weighs 70,000 grains, or 10 lb. English, and a liter of water weighs 1,000 grams, or 1cc. = 1 gram.

As a neutral solvent water is unsurpassed, and it dissolves all gases to a greater or less degree. If no chemical action takes place between the gas and the water the amount absorbed depends upon—(1) the nature of the gas; (2) the temperature of the water; and (3) the pressure under which the absorption is effected.

1. Some gases are much more soluble than others; a given volume of water at 0° C. will dissolve 1,149 times its own volume of ammonia gas, but only .019 of hydrogen.
2. The cooler the liquid the more gas will it dissolve; hydrogen, however, is an exception to this rule, as between 0° C. and 25° C. water dissolves .019 of its own volume of the gas without regard to temperature.
3. The volume of the gas absorbed varies directly as the pressure; that is to say, at all pressures the water absorbs the same volume of gas, but the volume of the gas varies inversely as the pressure.

This is taken advantage of in the manufacture of aërated waters. Carbon dioxide gas is absorbed by water under pressure, the amount dissolved depending upon the pressure; this pressure is then kept constant by the bottle being corked and wired, but when the cork is removed the liquid is now under ordinary atmospheric pressure, and can only hold in solution the volume of gas corresponding to that particular pressure, the excess escaping and causing the effervescence.

The solution of solids, like the solution of gases, depends largely upon the nature of the solid; 1 liter of water will dissolve 0.14 grams of strontic sulphate and nearly 1,000 grams of magnesic sulphate.

The rate of solution is affected by the fineness of division and by agitation of the liquid, as, if the liquid be quite still, the layer of water next the solid becomes saturated, and being therefore denser protects the remainder, solution only proceeding by liquid diffusion, a process infinitely slower than gaseous diffusion.

The solubility of a salt, as a rule, increases with the temperature of the water, but strontic sulphate and lime are exceptions, being more soluble in cold than hot water.

When a point is reached at which no more of the solid can be dissolved, the liquid is said to be saturated, and if allowed to stand so that the water can cool or evaporate, the solid will again separate out—often in the crystalline form, and this form is in many cases due to water held in a feeble state of combination, and called water of crystallisation. For instance, sodium carbonate crystallises with 10 molecules of water of crystallisation, and these crystals when exposed to air effloresce, that is, give off some of their water, and crumble down to a white powder.

The solution of a solid in water is generally accompanied by a lowering of temperature, caused by the conversion of sensible into latent heat, when the substance passes from the solid into the liquid state, and in the same way when the substance crystallises the heat so rendered latent reappears. In the case of some oxides and anhydrous salts, solution is accompanied by a rise in temperature and this is caused by the water forming a definite combination, heat being generated by chemical action. When many oxides of the metals are brought in contact with water they combine with it forming a body called a hydrate.

Calcic oxide		Water		Calcic hydrate.
$Ca\,O$	$+$	H_2O	$=$	$Ca(HO)_2$.
Sodic oxide				Sodic hydrate.
Na_2O	$+$	H_2O	$=$	$2(Na\,HO)$.
Potassic oxide				Potassic hydrate.
K_2O	$+$	H_2O	$=$	$2(KHO)$,

and the water which so combines with the metallic oxide to form a hydrate is called water of hydration.

Water is always undergoing a process of circulation in Nature, and in this way is one of the most important factors in the change of the face of the globe, and also in regulating the temperature and preserving health.

The atmosphere, especially over the sea, contains a large amount of water vapour in suspension, and the amount which it can so hold is dependent upon the temperature of the atmosphere; the hotter it is the more aqueous vapour can it hold, whilst any lowering of the temperature of the air causes a deposition of some of the suspended vapour as rain, dew or fog.

The weight of any volume of aqueous vapour is about $\frac{6}{10}$ths of that of an equal volume of air, hence air highly charged with aqueous vapour is lighter than dry air, and rises, and as it ascends the air and water vapour expand, being under diminished pressure, this expansion gradually cooling it; also in the higher regions it meets currents of air cooler than itself, or it may come in contact with the tops of mountain ranges, any of which causes by rapidly cooling the air force it to deposit some of its water vapour, and this forms little bubbles, which, being full of water vapour and therefore lighter than the air, are kept floating as clouds until something causes the contraction of the little vesicles and the water comes back to the earth as rain. When this condensation of water vapour happens near the surface of the earth, the result is mist, fog and dew. There are three distinct forms of cloud, the "Cirrus," the "Cumulus" and the "Stratus."

The little flecks of delicate cloud which are always seen at the greatest height are the Cirrus, then we have the bold rounded masses of white cloud which are the Cumulus, and finally the horizontal sheets of cloud nearest the earth, which we call the Stratus. These forms often run into one another and are known as "Cirro-stratus," "Cirro-cumulus," and

"Cumulo-stratus;" this latter is the densest form of cloud and includes what is known as the "Nimbus"—the heavy black thunder cloud.

When the temperature of the upper regions of air is below the freezing point, the moisture as it condenses, freezes and descends as snow, which, if examined under the microscope, is seen to be composed of most exquisitely formed crystals; whilst if the rain drops after they are formed pass through a region of air below the freezing point, we have the formation of hail.

When the little bubbles of water of which the clouds are formed condense and fall as rain, in their passage through the air they dissolve some of the more soluble gases with which they come in contact, such for instance as ammonia, traces of nitric acid, small quantities of oxygen and carbonic acid, also traces of any local impurities which may be present in the air from manufactories or towns, such as hydrochloric, sulphurous and sulphuric acids.

The rain falling on the ground partly evaporates, partly runs off and partly sinks in, the relative amounts varying with the configuration and density of the ground.

In the magnesian limestone districts, about 20 per cent. penetrates; in the new red sandstone, 25 per cent.; in the chalk, 42 per cent.; and in the loose tertiary sand, 90 to 96 per cent. Sinking into the ground, the water comes in close contact with considerable quantities of carbonic acid generated from the decaying vegetable matter in the subsoil, and it absorbs a considerable quantity of this gas, and then penetrates more or less deeply into the ground, dissolving anything it can take up, either by its own solvent properties or by the solvent power of the carbonic acid it contains. The carbonic acid so present in the water causes it to be fresh and sparkling, and where there is a deficiency of carbonic acid, and in some sandy soils, there the water is flat and unpalatable.

The water sinks through the soil until it comes to some strata which it cannot penetrate, and here it collects and finds its way to the surface in the form of springs, the water being laden with the various salts it has met with and dissolved in its passage through the earth. The springs form rills, and these are swelled by the rain which runs off from the surface of the soil, and this surface drainage brings with it more impurities, chiefly held suspended in it, such as dead leaves, dust, mud, &c. The rills increase in size, becoming streams, and join the rivers, which again flow back to the sea.

The sea may be looked upon as Nature's evaporating basin, as here, under the influence of the sun's rays, the pure water is once more converted into vapour, once more to go through its round of operations, whilst the salts it has dissolved from the earth, and the suspended matter it has swept down from the surface of the land, remain behind, and in the course of centuries build up fresh continents. From the moment the rain reaches the soil it is the great agent of geological change, and is always at work, dissolving out and washing away the existing land, only to build it up in fresh places ; the amount of solid matter so removed by the rivers of the world amounting to millions of tons daily.

In falling from the clouds, the rain performs the important function of collecting the ammonia and nitric acid necessary for plant life, and brings them down to the plants in the condition in which they can be most readily assimilated ; whilst in its passage from the springs to the ocean it washes away those waste products of animal life which, if they were allowed to remain, would breed pestilence and general decay ; if the free flow of the rain and spring water be interrupted, stagnant pools and swamps, breeding disease and exhaling malaria, are the immediate result. The circulation of water in Nature is of the utmost importance in regulating the temperature. Water vapour rises most abundantly in the tropics, and in its evaporation renders latent an immense amount of heat, and this heat is again given out whenever the water vapour again undergoes condensation into rain. In this way water vapour tends to equalise the temperature of the earth, by carrying heat from the places where it is in excess to those places where it is wanted.

There is no such thing in Nature as pure water. In passing through the atmosphere, the rain becomes highly charged with gases, taking up from 3 to 30 cubic centimeters per liter; the oxygen is found in larger proportions than in air, reaching as much as 38 per cent. of the total amount of dissolved gas. It also contains about 3 per cent. of carbon dioxide and minute traces of carbonate and nitrate of ammonia, besides small particles of solid matter, such as dust (especially in very windy weather), salts, and organic matter. In the country, where the air is fairly clean, rain water owing to its purity and great aëration is both wholesome and pleasant to drink, but in or near towns the soot and dirt derived from the air and roofs make it unfit for drinking purposes.

Spring water contains most of the gaseous impurities present in rain water, and beside these all the mineral impurities it has dissolved in its passage through the ground.

The most ordinary impurity of spring water is chalk or calcic carbonate, which gives the properties which we call "hardness," a hard water being a water containing calcium and magnesium salts in solution.

Pure water cannot dissolve calcic carbonate, but when it filters through decomposing vegetable matter, it dissolves carbonic acid gas, which is produced by decaying leaves, &c., and water containing carbonic acid dissolves chalk; hence, when such water filters through or over chalk beds, some is dissolved, and the water becomes hard.

There are two kinds of hardness in spring water, "temporary hardness" due to calcic and magnesic carbonate dissolved by the carbonic acid in water, which can be got rid of by any method which will drive off or neutralise the carbonic acid; and "permanent hardness," due to the presence of any soluble salts of calcium or magnesium held in solution by the solvent properties for the water itself.

In chalk districts, where the water is very hard, it is rendered soft by removing the carbonic acid holding the chalk in solution, by adding to such water some lime-water, which is a solution of calcic hydrate. The calcic hydrate combines with the carbonic acid, forming calcic carbonate; and this is precipitated, together with the original calcic carbonate, which, no longer having any carbonic acid to hold it in solution, falls down as a white powder. This is called Clarke's process for softening water.

Water containing one grain of calcic carbonate in a gallon of water is said to have one degree of hardness.

Besides calcic carbonate and sulphate, we find in spring water the sulphates, carbonates, chlorides and nitrates of magnesium, potassium, sodium, manganese, and iron, and also small quantities of organic matter and occasionally silicates.

In spring waters the constituents vary very much in quantity according to the soil through which they have filtered, and they may be classified according to the chief constituent they contain, into (1) Waters in which the saline contents are chiefly carbonates, such as the waters of Vichy, Ems and Spa. (2) Waters in which the salts are mostly sulphates, such as the waters of Carlsbad, Epsom and Bath. (3) Waters in which the salts are chiefly chlorides, like the waters of Wiesbaden, Leamington, Harrowgate, and Cheltenham. (4) Waters in which the chief salts are silicates, like the hot springs of Iceland.

When the water of a spring is so highly charged with saline or gaseous impurities as to be unfit for ordinary purposes, it is called a "mineral water."

The gases contained in spring waters vary very much in quantity; in some cases the amount is small, whilst in others the water having filtered through subterranean caverns containing carbonic acid or other gases under considerable pressure, the water has dissolved so much that when it escapes into air under the ordinary pressure it liberates some of the gas and effervesces.

In some springs sulphuretted hydrogen is found dissolved, which gives the water the odour of rotten eggs.

River water, although it contains a large proportion of spring water, has generally a smaller quantity of dissolved solids in it, and this is partly due to its being largely diluted with surface water, which contains very little dissolved solid matter, and partly to the fact that water in flowing through the air gives up some of the carbonic acid it contains and deposits calcic carbonate.

In river water we find, besides the dissolved mineral and gaseous impurities of spring water, dissolved organic substances derived from drainage discharging into the streams and also from decaying vegetable matter, and this organic matter gradually undergoes a process of purification being oxidised by the oxygen dissolved in the water and gradually converted into carbonic acid, water, nitrates, nitrites, and ammonia.

In addition to the dissolved solids and gases found in river water, there is also a quantity of waste matter in a state of suspension, generally known as suspended solids, consisting of small particles of insoluble matter carried into the rivers by the surface drainage.

The part played by the rivers of the world in changing the face of the globe may be imagined from the fact that in suspended matter alone the Amazon discharges into the sea over 950 million tons of solids per annum, and it has been estimated that the suspended matter annually discharged into the sea by the Mississippi is equal to 4,000 million cubic feet of clay, and that the quantity thus conveyed into the Bay of Bengal by the Ganges and Brahmapootra amounts to ten times as much.

Sea water is, to all intents and purposes, a mineral water of the third class, its principal constituent being sodic chloride, besides which it contains a large number of other salts, chiefly chlorides and sulphates of sodium, magnesium, potassium and calcium.

The amount of solid matter varies but little in different parts of the ocean; at the poles it is perhaps a little less saline on account of the large quantity of fresh water formed by the melting of icebergs, whilst at the equator it is a little more saline on account of rapid evaporation. In inland seas, where the evaporation is very great and the quantity of water supplied by rivers not very large, the proportion of dissolved solid matter present is generally far above the average, as may be seen in such cases as the Dead Sea, and to a much smaller extent in the Mediterranean.

SALTS IN SPRING, RIVER, AND SEA WATER.

In grains per gallon.

	Spring.	River.	Sea.
Calcic carbonate	16.30	10.80	3.32.
Calcic sulphate	5.37	3.00	93.21.
Magnesic carbonate	0.00	1.25	trace.
Magnesic chloride	0.00	0.00	220.55.
Magnesic sulphate	0.93	0.00	144.62.
Sodic chloride	2.64	1.80	1850.74.
Silica, alumina, &c.	0.23	0.27	trace.
	25.47	17.12	2312.44

The extraordinary differences in the composition of river and sea water at first sight do not appear compatible with e theory that sea water is usually concentrated river water. f we compare the analyses of a river water and the sea near s mouth, it is seen that those substances brought down by e river in greatest abundance, such as the carbonates of me and magnesia and silica, are present in the sea water in e smallest quantity, these substances being abstracted from e water by marine animals and plants to form their shells nd structures.

HYDRIC DIOXIDE.

Hydrogen and oxygen form a second compound, in which 2 parts by weight of oxygen are combined with 2 of hydrogen nd the hydric dioxide or peroxide therefore has the formula $_2O_2$. It is a colourless, syrupy liquid, when concentrated, ith strong bleaching properties, due to the ease with which e second atom of oxygen is liberated from the molecule of e dioxide; it whitens the skin and decolorises the hair, and r this reason is used as "Golden wash" or "Golden hair ye," when it oxidises the colouring matter and so partially estroys it. It has a specific gravity of 1.43 and slowly de-omposes at 21.1 °C. into water and oxygen, the decomposition creasing in rapidity as the temperature rises.

It is neutral to test papers and bleaches litmus solution. he most convenient method of preparing it is to pass a stream well washed carbon dioxide through baric dioxide (BaO_2) spended in water:—

Baric dioxide		Carbon dioxide		Water		Baric carbonate		Hydric dioxide.
BaO_2	+	CO_2	+	H_2O	=	$BaCO_3$	+	H_2O_2.

he carbon dioxide is generated from marble and hydrochloric id in the bottle (A,) (Fig 24), and is washed by being made to bble through water in the wash bottle (B), which frees it om any traces of acid which might be mechanically brought er by the gas, and it is then passed through the baric dioxide suspended in water in the cylinder (c). The baric carbonate formed gradually settles down to the bottom of the cylinder, and the dilute solution of hydric dioxide can then be concentrated by evaporation over sulphuric acid in vacuo.

When hydric dioxide is brought in contact with finely divided metals, such as silver, gold or platinum, it is decomposed and oxygen is liberated, the metals themselves undergoing no change.

Silver		Hydric peroxide		Silver		Water		Oxygen.
Ag	+	$2(H_2O_2)$	=	Ag	+	$2(H_2O)$	+	O_2.

It bleaches litmus and indigo by oxidising them, and will also oxidise arsenious and sulphurous acids into arsenic or sulphuric acid.

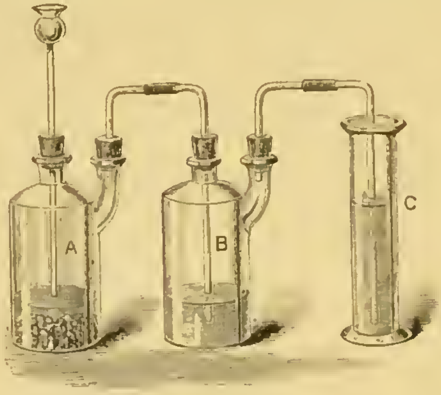

Fig. 24.

Sulphurous acid		Hydric dioxide		Sulphuric acid		Water.
H_2SO_3	+	H_2O_2	=	H_2SO_4	+	H_2O.

When the peroxides or oxides of certain metals are added to hydric dioxide, both oxides undergo decomposition at the same time:

Silver oxide		Hydric dioxide		Silver		Water		Oxygen.
Ag_2O	+	H_2O_2	=	Ag	+	H_2O	+	O_2.

Manganese dioxide		Hydric dioxide		Manganese oxide		Water		Oxygen.
MnO_2	+	H_2O_2	=	MnO	+	H_2O	+	O_2.

In all these cases the action is rendered more rapid by the presence of alkalis and retarded by acids.

Hydric dioxide may be detected by adding to the solution supposed to contain it, a few drops of chromic acid, which is oxidised, forming a blue solution containing an unstable perchromic oxide. If only small quantities of it are present, the solution is then shaken up with ether which dissolves the blue compound, and rising to the surface of the liquid renders it visible. Hydric dioxide will also turn a solution of potassic iodide and starch blue, by liberating the iodine which then forms the blue iodide of starch.

CHAPTER VI.

DRINKING WATER.

Natural impurities and their effect upon health—Sewage contamination—Sources of drinking water—Purification of water—Flitration on the large scale—Porter-Clark process—Anderson process—Anti-Calcaire—Domestic and Ship filters—Filtering media—Animal charcoal—"Spongy iron"—"Carbalite"—"Manganous carbon"—"Silicated carbon"—The management of filters—Ready methods for the purification of water.

THE natural impurities of water may be classified as gases, dissolved solids, and suspended solids; and these nearly all exert a certain amount of influence upon our health, but the action is very slight, and it is only the constant drinking of the same water over very long periods that makes the result noticeable; for instance, there is no reasonable doubt that water containing sulphate of lime produces dyspepsia, and should be avoided, not only for that reason, but because it is suspected of being connected with gôitre and calculous affections common in those districts where the water supply is derived from the limestone rocks; but at the same time, such water is usually very free from natural organic impurities, and it may take years to develop the other effects; but besides these natural impurities there are other sources of contamination to which water is exposed, of a much more dangerous description, the worst being sewage contamination; whilst in rare cases a water may become charged with dissolved metallic impurities, such as lead or copper.

A water may become contaminated with sewage either by eakage from a cesspool situated in the vicinity of a well, by eakage into water pipes in sewage laden ground, or by ontamination of water in cisterns from sewer gas, due to the verflow from the cistern leading into the drains; such con-amination nearly always produces diarrhœa, and often typhoid ever, whilst in hot climates it causes dysentery and cholera. n Nature, to a great extent, organic contaminations of this haracter in rivers and streams are destroyed and rendered nnocuous by the oxidising action of the air dissolved in the ater, the oxygen converting the organic impurities into arbonic acid and nitric acid; but in confined spaces, such as isterns and wells, this can only take place to a very small xtent, and we must therefore consider the means by which uch water can be rendered as little injurious as possible to ealth.

The chief sources of water are: (1) Rain water collected om the roofs, &c., and this, in the country is pure and soft.) Water from shallow wells; this is nearly always bad, and more exposed to sewage contamination than any other kind water. (3) Springs; these are fairly free from organic matter though often very hard. (4) River water, which is made to ass through depositing and filtering tanks; this water has the sadvantage of having been contaminated with sewage and ther impurities, so that there is a risk that if the purification ocess failed at any time, the impure water would be supplied r drinking. (5) From deep wells, the water from which is nerally free from organic impurities but very hard. The ater obtained from any of these sources is supplied to the ouse by one of two methods—either by intermittent or nstant service.

The advantages of the constant service, in which the pes distributing the water are always kept charged, are very eat, as the necessity for cisterns is done away with, and the pes being always full of water, are not liable to corrode as when they are alternately full of water and air, whilst the chances of sewage contamination from leaky pipes, &c., is very much diminished. In the intermittent water supply, the water is only turned on for a short time in the twenty-four hours, and it is necessary therefore to have cisterns which will hold a sufficient supply for the house, and which frequently become contaminated with dust, vegetable growths, and sewer gas, unless precautions are taken to prevent it.

Gaseous impurities in water can be got rid of by long boiling, which also tends to kill many of the organisms to be found in water.

Dissolved solids, such as common salt, calcic sulphate, and Epsom salts, can be got rid of by distillation—that is by converting the water into steam, which escapes, and which can then be condensed into water by cooling it, leaving the salts behind.

Suspended solids, and under certain circumstances some of the other impurities as well, can be got rid of by filtration through various media.

In the purification of water by filtration for drinking purposes on a large scale, two distinct means are employed for the removal of foreign matter, viz., mechanical and chemical. The mechanical processes as employed by most of the large water companies, consist of allowing the heavier impurities to subside in large reservoirs called settling tanks, and then passing the partially clarified water through filtering beds from six to eight feet in thickness built up in layers of gravel and sand of varying degrees of coarseness, through which the water filters at the rate of from 60,000 to 100,000 gallons per hour per acre of filter bed. In this process very little, if any, organic matter is destroyed by oxidation, the removal being purely mechanical, and due to the retention, chiefly by settling, of the fine particles of suspended matter during the passage of the water through the bed. In such lter beds the sand employed must be clean and the grains f medium size—the presence of too fine a sand only serving choke the pores of the filter bed—and it is absolutely mperative that the top layers of sand, which have to bear the eaviest portion of the work, should be frequently replaced y fresh, well washed sand, whilst the whole bed should be enewed with carefully washed material at least every two years.

The drawbacks to this kind of filtration are that an ncrease in the rate of flow through the bed is sufficient to arry the deposited matter through the filter, whilst the area equired is of necessity very large, and the smaller forms f organisms are not removed.

Of the processes which combine chemical with mechanical ction, the "Porter-Clark" process may be taken as a type. n this system lime water is mixed, by means of agitators, ith the water to be purified, and by combining with the arbonic acid in the water, causes a deposition of the calcic arbonate as a very fine powder—the separation of the finely ivided carbonate also mechanically removing a large portion f the organic matter—and the water is then clarified by orcing it through a filter press in which frames covered y stretched canvas or other filtering media retain the solid articles.

In "Maignen's" process a powder called, "Anti-Calcaire," ontaining chiefly lime, sodic carbonate and alum, is added, the lum causes a coagulation and precipitation of the organic natter, whilst the sodic carbonate attacks the salts of lime nd magnesium.

In the "Anderson" process the action which iron has pon the organisms and organic matter in water is relied upon. When this process was first introduced, it was supposed to be ssential that the iron should be in the finely divided spongy condition, which is obtained by reducing it at low temperatures rom its ores, but it has since been found that scrap iron, when well agitated in contact with the water, answers the same purpose as well, if not better. The action here is probably mainly due to the formation of carbonates of iron by the carbonic acid in the water, and on exposure to air oxidation takes place, and causes a coagulation. Some other processes are in use to a small extent, and in nearly all, alkaline hydrates or salts are first added to neutralise carbonic acid and precipitate salts of lime and magnesium, and the precipitated matter is then removed by rapid filtration.

However well filtered or treated on the large scale water may be, the filtration of the water by the Companies should always be supplemented by the use of filters in the house, as there is always the risk of a break down in the filtration; whilst if the water be supplied in a state of purity, storage in rarely cleaned cisterns, in most cases again pollutes it before use, and under many conditions as on board ship or in country places, filtration on a small scale is the only purification a water undergoes. In domestic and ship's filters, the media which used to be employed consisted up to thirty years ago, almost entirely of substances which mechanically kept back the larger suspended impurities, such as sponge, sand, or indeed anything of which the pores were sufficiently small to retain visible impurities, whilst in latter years the use of materials exercising a chemical, as well as a mechanical action upon the foreign matter have come largely into use.

Of these materials the most effective are undoubtedly carbon, in its various forms and the so called spongy iron.

Carbon owes its high position as a filtering agent to a combination of properties which occupy the border land between chemical and physical action; a freshly burnt piece of charcoal has a wonderful power of absorbing gases, a cubic inch of the substance being able to compress into its pores 100 times its own volume of ammonia gas, whilst it absorbs other gases to a smaller extent. The gases so compressed are rendered excessively active in their chemical ffinities, so that if a piece of freshly burnt charcoal be xposed to the action of sulphuretted hydrogen, until it as absorbed as much as it will of this gas, and be then lunged into oxygen, it is not unusual for the charcoal to urst into vivid combustion owing to the rapid conversion of he sulphuretted hydrogen in its pores into water and sulphur ioxide—hence the enormous value of charcoal for respirators, ewer traps, and deodorising animal matter which has com- nenced to putrify. This power of absorption which charcoal ossesses is not confined to gases, for many liquid and solid ubstances are removed from solution in water by its means, nd the most active form of carbon for this purpose is that which held in an almost molecular state of division on the surface f mineral matter. When bones are heated out of contact with ir, the organic matter which they contain is broken up and ne carbon is left deposited in this fine state of division upon ne calcic phosphate and calcic carbonate which form the nineral structure of the bone, and the substance so formed oes by the name of bone black or animal charcoal. If some f this substance be shaken up with port or claret, and the nixture be then filtered, it will be found to be rendered olourless, an effect due to the abstraction of the colouring atter by the carbon ; the colouring matter however, seems nly to have entered into very weak combination, if any, with e carbon, as it can be recovered by washing the bone black ith a weak alkaline solution.

Bone black contains only 10 per cent. of pure carbon, and et from the fineness of its state of division, it is far more ctive than wood charcoal containing 90 per cent. and upwards.

When a water containing organic impurities is filtered rough a finely divided carbon of this description, the organic atter is partly mechanically taken from it and partly estroyed, burnt up by the oxygen held by the carbon, and for this reason animal charcoal filters were long looked upon as perfect water purifiers; but in 1878, it was pointed out by the Royal Commission on River Pollution, that it had the serious drawback, that when water which had been filtered through it was allowed to stand, minute organisms, both animal and vegetable, made their appearance in the water and rendered it not only unfit to drink but actually offensive. Whilst if the animal charcoal has not been burnt at a sufficiently high temperature, which is rarely done, as it means a certain loss of carbon, some of the nitrogenised organic matter of the bone remains and becomes a breeding place for myriads of minute organisms which find their way into the water. Also fresh organic matter like the white of an egg (albumen), which has not yet entered into putrefactive change, passes through animal charcoal almost unacted upon.

In spite, however, of these drawbacks, the purifying action on water to be used at once is so marked, that animal charcoal still retains its place at the head of the filtering media; attempts being made, however, in the best forms of filters to remove its power of supporting animal and vegetable life by the previous treatment of the animal charcoal with acids which dissolve some of the calcic phosphate contained in it, and considerably reduce the chance of its giving rise to the lower forms of organisms.

Spongy iron used in Bischof's filters is made by reducing haematite and other iron ores by carbon at a low temperature so as to avoid fusing the particles together, and to present as large a surface as possible to the water.

The power of metallic iron to purify water has been known for a long time, and it is a well recognised fact that if a ship takes in foul water, the impurities are greatly diminished by keeping the water in iron tanks for a sufficient length of time, the rolling of the ship helping the action by agitating the water and bringing fresh portions in contact with the etal; and as early as 1857 it was proposed to purify water y suspending in it bundles of iron wire, and to leave them in ontact for a couple of days—about 1 lb. of iron being used to oo gallons of water—a process which gave good results, hilst the increase in surface given by using the iron in e spongy state renders the filtering and purifying action uch more rapid.

The organic germs and impurities in water mostly consist f the four elements, carbon, hydrogen, oxygen and nitrogen, nd during the natural purification of a water by dissolved xygen, the organic matter is broken up, burnt by slow ombustion, and the carbon forms carbon dioxide, the hydro- en water and the nitrogen, nitrites and nitrates—an action hich fresh animal charcoal and iron both seem to accelerate.

In the spongy iron filter the water dissolves a certain roportion of iron, and in order to remove this the water is ade to pass through a layer of fine sand and black oxide of anganese, which precipitates and retains the iron as ferric ydrate.

In Maignen's “Filtre Rapide,” animal charcoal which has ndergone a preliminary treatment with acetic acid and then eutralisation with lime water is employed, whilst great apidity of filtration is effected by using a cone covered with sbestos cloth and thus greatly increasing the filtering surface.

In the service we are fortunate in having perhaps the best orm of filter extant. The filtering medium is neither animal harcoal or spongy iron, but an artificial compound called “Carbalite,” which possesses the best characteristics of both edia, and whilst having all the decolourising and purifying owers of animal charcoal, yet from the absence of any hosphates or nitrogenised animal matter, it in no way tends o produce low forms of life, and also, containing iron, it by he dual action removes organic matter and purifies water far ore effectively than any other filter examined. Another great advantage is that the mass of filtering material present is very large, the efficient filtration not being sacrificed to elegance of form as is generally the case in domestic filters.

In the form generally used in the Navy, the filter is usually fitted in the bottom of a water tank holding from 200 to 600 gallons (Fig. 25), and the water filters down through one thickness of the carbalite, and up through a second layer into a compartment from which the filtered water can be drawn. In the smaller form for domestic use, the water simply passes down through the carbalite, and collects in the space below it (Fig. 26).

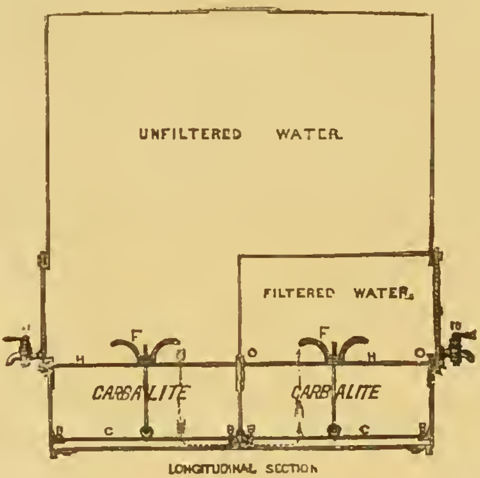

Fig. 25.

The form of the filter is convenient, as by unscrewing the bolt (F) the plate (HH) can be removed, and the carbalite taken out and cleaned, or new carbalite put in, whilst the rate of filtration can be regulated by screwing up or loosening the bolt. If a water is fairly clean, the bolt is loosened and rapid filtration ensues; whilst if the water is very dirty, the screw is tightened and the top plate compresses the carbalite and causes slow filtration.

The relative value of "carbalite" and animal charcoal in destroying organic matter was tested by taking two filters of equal capacity, and charging one with carbalite and the second ith animal charcoal, equal quantities being used; the animal arcoal being the purified and prepared form used in Maignen's lters, and being aided in its action by an admixture of some ery finely divided carbon which has been found to render the lters more efficient. Water taken from the Thames at reenwich was filtered through these in equal quantities, and a fairly rapid rate of flow, for several days, and then alyses of the filtered waters were made, the organic matter

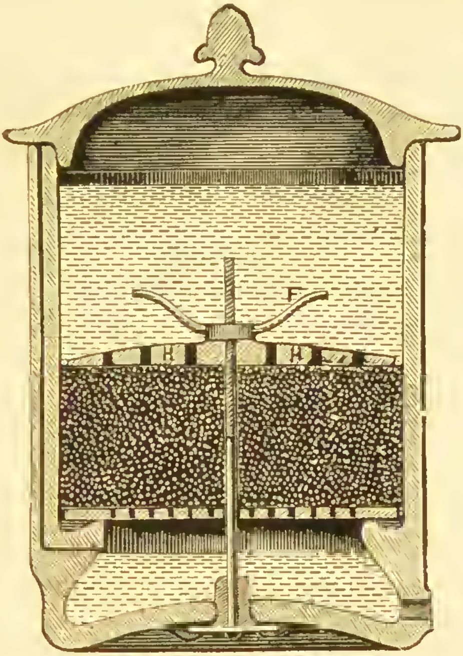

Fig. 26.

ing determined as free and albuminoid ammonia in parts r million, whilst the total solids and chlorine were determined grains per gallon.

EFFECT OF FILTRATION.

		After filtration through	
	Thames water before filtration.	Carbalite.	Animal Charcoal.
otal solids ...	... 110.50 ...	... 80.50 ...	... 76.50
hlorine ...	... 42.90 ...	... 32.20 ...	... 30.30
ree ammonia	... 2.70 ...	... 0.64 ...	... 1.70
buminoid ammonia	1.36 ...	... 0.10 ...	... 0.17

Showing that the carbalite had removed 80 per cent. of the organic impurities present, whilst the animal charcoal had removed 54 per cent. In Doulton's "Manganous carbon" filter, the medium is a mixture of animal charcoal and black oxide of manganese which covers a block of prepared carbon through which the water has to pass. The black oxide of manganese is here supposed to undergo partial reduction, and by giving up oxygen, to more actively attack the organic matter.

Besides the filters mentioned, there are several others, such as the Silicated Carbon filter in which a block of prepared carbon is used, and is covered by the powder of silicated carbon made by heating shale or other carboniferous substance with clay out of contact with air. No filter should be used which relies for its action upon a block of carbon alone, as the suspended impurities in water deposit upon it and form a slime upon the exterior, which not only checks the filtration, but in many cases contaminates the water it is supposed to purify.

In using a domestic filter it must be remembered that besides its chemical action, it is practically a dirt trap, and that when once the pores of the carbon are choked with impurities taken from the water which has passed through it, all chemical and mechanical action ceases, whilst the carbon renders it impure instead of removing foreign matter.

This point has been made clear during the last few years by the researches of Dr. Percy Frankland in the biological examination of waters, and he has shown, by determining the number of micro-organisms in water before and after filtration, that at the end of a month at latest, animal charcoal tends to multiply to an enormous extent the number present, although for twelve days or a fortnight it entirely removes them; and although it is possible to take micro-organisms into the system without any effect on the health when they are of a harmless kind, yet a filter which allows harmless germs to pass, will also allow the germs of cholera and typhoid fever to go through unchecked. This shows that frequent cleansing and renewal of the filtering material in all forms of filters is an absolute necessity; in ordinary charcoal filters this should be done every three weeks at least to ensure safety, whilst even with spongy iron and carbalite, four to six months is the outside period during which they can with safety be continuously used.

On board ship distillation of sea water is commonly resorted to in order to render salt water fit for drinking, and although the water so obtained is pure, yet all gases having been driven from it by the boiling, it is insipid for drinking purposes until it is again aërated.

This is best accomplished by allowing it to trickle slowly down through a long column of wood charcoal or carbalite up which air is passing

In many cases, such as during expeditions up rivers, etc., when away from the ship, the use of regular filters is impossible, whilst the water derived from swampy ground, marshes, or streams full of vegetable matter, is quite unfit for drinking purposes, and tends to produce dysentery and other diseases of the same kind. Under these conditions a rough filter may be constructed, by sinking an old cask, charred on the inside and with some holes bored in the bottom, in the bed of the stream, and putting into it fine gravel and the cleanest sand to be found, in a layer 6 to 8 inches thick, and if possible below the sand a layer of charred wood from the fire; a thin layer of gravel on the top of the sand will keep it from rising with the water and for several days such a filter will prove most effective.

Where even this is impossible a few grains (6 per gallon) of alum added to the water, or boiling the water with the leaves left after making tea, serve to cause the organic matters present to clot together and settle out, leaving the water considerably purified.

Exposing the water to the action of air, whilst in finely divided streams is also very efficacious in removing offensive organic vapours and sulphuretted hydrogen from water, and also to a certain extent organic matter; this is best done by pouring the water several times through a fine sieve, held as high as possible above the vessel which is to catch the aërated water.

The determination in a rough way of the purity and fitness for drinking of a water, is as a rule perfectly useless, as the presence of the more easily detected impurities may indicate the presence of organic contamination of the worst kind, or may be due to perfectly harmless circumstances. In selecting a water for drinking purposes, it is essential to know the source and history of the water as well as the nature of the impurities in it, before any conclusion can be come to, as to its effect upon health. For instance, the presence of considerable quantities of chlorides in a shallow well water would at once condemn it as a drinking water, the chlorides being almost certainly derived from sewage, whereas the presence of the same amount of chlorides in a deep well water would not be any proof of its being unfit for drinking purposes, having most probably been derived from soluble chlorides in the beds through which the water has filtered.

CHAPTER VII.

BOILER INCRUSTATION.

Saline constituents of fresh and sea water--Incrustations from different kinds of water—Causes of boiler incrustation—Calcic carbonate —Calcic sulphate—Solubility—Effect of concentration on sea water—Effect of temperature and pressure on the saline constituents of sea water—Formation of magnesic hydrate in marine boiler deposits—Action of distilled water on boilers—Waste of fuel entailed by boiler incrustation—Prevention of incrustation—Anti-incrustators—Chemical and mechanical action of anti-incrustators—Zinc in boilers—Feed water heaters.

WHEN a natural water is boiled and the carbonic acid which it contains is expelled, the carbonates of calcium, magnesium and iron which are only held in solution by water in the presence of free carbonic acid, are thrown down; and as the remaining water in the boiler becomes more and more concentrated by the escape of steam, so the calcium sulphate which is but slightly soluble in water is also deposited, and with the separation of these mineral salts, organic matter which the water may contain is also to a certain extent mechanically carried down, and these various bodies forming in thin cohesive layers on the sides and bottom of the vessel give rise to the so called fur in a kettle, or the more serious boiler deposit.

This deposit being a bad conductor of heat delays the boiling of the water, and by allowing the metal to become unduly heated, gives rise to "burning" of the boiler plates, whilst if the deposit be thick the plates may become red hot, and then should the deposit crack and allow the water to reach them, the sudden and rapid evolution of steam often results in explosion, whilst in any case the life of the boiler is much shortened by corrosion and over heating.

Fresh water is very variable in composition, but, as a rule, contains as its chief saline constituents the carbonates of lime and magnesia, held in solution by carbonic acid present in the water, and also small quantities of the sulphates of these metals, and traces of common salt.

Sea water contains a far higher proportion of saline matters in solution than fresh water, and also in totally different proportions, as although sea water is only river water concentrated by the evaporative power of the sun's rays during long ages, yet, owing to the deposition of calcic carbonate during the flow of the water down rivers, and also to its being used by certain forms of marine life, calcic carbonate (carbonate of lime), which is the chief saline constituent of fresh water, is reduced to a mere trace in salt water, whilst the salt has become the all important constituent, and the sulphates of lime and magnesia, together with chloride of magnesium, are also present.

The wide difference in composition of fresh and salt water may be seen from the following analyses:—

SALTS IN SOLUTION IN RIVER AND SEA WATER.
GRAINS PER GALLON.

	River water. THAMES.	Sea water. LOWESTOFT.
Calcic carbonate (chalk)	10.80	3.9
Calcic sulphate (gypsum)	3.00	93.1
Magnesic sulphate	0.25	124.8
Magnesic chloride		220.5
Magnesic carbonate	1.25	trace
Sodic chloride (salt)	1.80	1850.1
Silica (sandy matter)	0.56	8.4
Oxides of iron and alumina	0.27	trace
Organic matter	2.36	trace
	[illegible]	[illegible]

In the older forms of marine boilers, working at comparatively low pressures, sea water was almost universally employed; but with the introduction of high-pressure tubular boilers the amount of deposit formed was so serious, and the difficulty of removing the incrustation from between the tubes so great, that it became almost imperative to discontinue the use of the sea water, and to rather accept the expense of supplying the boilers with distilled water, than risk the burning and destruction of the tubes and plates in inaccessible portions, where the deposit had to be allowed to collect until the time could be spared for a complete clean out and refit. But, after several years' experience of this system, it is found that the trouble has only been transferred from the steam boilers to the distilling apparatus, and that the enormous deposits formed in the latter cause them frequently to break down or become in some way or other unfit for use, so necessitating the introduction of sea water into the boiler to eke out the supply of distilled water from the condensers.

Distilled water is presumably free from all dissolved solids, but the condenser water always contains some of the lubricants from the cylinder; and in the days of animal and vegetable lubricators, or fat and oils other than mineral, this water, on account of the superheated steam breaking the oils up and liberating fatty acids, caused a large amount of damage to the plates of the boiler; but with the use of mineral oil lubricators of the right kind this trouble is done away with, and a slight coating of organic matter is, as a rule, the only incrustation found in a boiler using distilled and condenser water only.

The great difference existing between sea and fresh water would lead one to expect a wide difference also in the kind of deposit formed from them, and this is found to be the case, as the following analyses of incrustations formed in the boilers of steamers using fresh river water, the brackish water at the mouth of a river, and sea water respectively, show :—

	River.	Brackish.	Sea.
Calcic carbonate	75.85	43.65	0.97
Calcic sulphate	3.68	34.78	85.53
Magnesic hydrate	2.56	4.34	3.39
Sodic chloride	0.45	0.56	2.79
Silica	7.66	7.52	1.10
Oxides of iron and alumina ...	2.96	3.44	0.32
Organic matter	3.64	1.55	trace
Moisture	3.20	4.16	5.90
	100.00	100.00	100.00

These may be taken as typical deposits, and show that with fresh water the incrustation may be looked upon as consisting of calcic carbonate, with small quantities of other compounds; that with a mixture of fresh and salt water the deposit consists of nearly equal parts of the calcic carbonate and sulphate; whilst the sea water gives practically pure calcic sulphate.

The presence of calcic sulphate exercises a very marked influence upon the condition and physical properties of the incrustation, as, under the conditions in which it is formed in a boiler, it separates in a crystalline form, and binds the deposit into a hard mass, an action which is also aided by the presence of magnesic hydrate.

A deposit consisting of calcic carbonate only, or of calcic carbonate and traces of the oxides of iron and alumina, sodic chloride, &c., is separated as a soft powder, which remains suspended in the water for some time, and which can fairly easily be removed from the boiler on cleaning; whilst, if calcic sulphate is present, the scale is extremely hard, and generally requires the use of hammer and chisel to detach it from the plates and tubes, an operation which is extremely injurious, and tends to shorten the life of the boiler.

The three principal constituents of boiler incrustations may therefore be looked upon as calcic carbonate, calcic sulphate, and magnesic hydrate, and the causes which lead to their deposition must now be considered.

Calcic carbonate is practically insoluble in pure water, that is to say, it requires more than 10,000 parts of pure water to dissolve one part of the carbonate;[*] but carbonic acid, which is present in all natural waters, when in contact with calcic carbonate converts it into bicarbonate, which is soluble, and this forms the so called "temporary hardness" in fresh waters. On heating such a water the bicarbonate is decomposed, carbonic acid gas escapes, and the calcic carbonate being insoluble, is deposited. Calcic carbonate is slightly more soluble in saline solutions, such as sea water, than in pure water, but the difference is so small that the above may equally be looked upon as applying to fresh and salt water.

Calcic sulphate is to the marine engineer the most important constituent of boiler incrustation, and its separation as a deposit from water is dependent upon a totally different class of phenomena to those which bring about the precipitation of calcic carbonate. Calcic sulphate is dissolved in water by the solvent power of the water itself, and not through the agency of carbon dioxide, and therefore merely boiling water at ordinary pressures does not suffice to cause its deposition, and for this reason it forms, together with soluble magnesium salts, the "permanent hardness" of fresh water.

The solubility of calcic sulphate in pure water varies very considerably with the temperature.

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[*] Soluble in 16,000 parts pure water according to Brande; 12,858 according to Kremers; 16,000 to 24,000 according to Buchholz.

100 parts of Water, at a temperature of		Dissolve calcic sulphate.
32° F. or	0° C.	0.205
41° ,,	5°	0.219
53.6° ,,	12°	0.233
68° ,,	20°	0.241
86° ,,	30°	0.249
95° ,,	35°	0.254
104° ,,	40°	0.252
122° ,,	50°	0.251
140° ,,	60°	0.248
158° ,,	70°	0.244
176° ,,	80°	0.239
194° ,,	90°	0.231
212° ,,	100°	0.217

Calcic sulphate is most soluble in water at 95° F. or 35° C. roughly, one part of calcic sulphate being dissolved in approximately 400 parts of water; and, inasmuch as the solubility of the salt is considerably decreased at 212° F. or 100° C., if a solution be taken saturated at 95° F. or 35° C., and then heated to 212° F. or 100° C., precipitation of a portion of the calcic sulphate will take place.

Calcic sulphate is much more soluble in a saline solution, such as sea water, than in fresh water, but its solubility rapidly decreases, (1) on concentration of the saline solution, and (2) on increase of temperature and pressure.

If ordinary sea water be concentrated, three distinct stages of deposition may be traced :—

(1) Deposition of basic magnesic carbonate.

(2) Deposition of calcic carbonate with remaining traces of the basic magnesic carbonate and hydrate: and, finally,

(3) Deposition of the calcic sulphate.

Whilst the variation in the saline constituents of the remaining liquid may be seen from the following table :—

SALINE CONSTITUENTS PER CENT.

Density	1.029	1.05	1.09	1.225
Sodic chloride	2.6521	4.4201	7.9563	23.8689
Calcic sulphate	0.1305	0.2175	0.3915	none
Calcic carbonate	0.0103	0.0171	none	none
Magnesic carbonate	0.0065	0.0032	none	none
Magnesic chloride	0·2320	0.3865	0.6960	2.0880
Magnesic sulphate	0.1890	0.3150	0.5670	1.7010

If the sea water be heated and concentrated above a density of 1.225, the salt commences to crystallise out.

The deposition of the calcic sulphate during the concentration of the sea water is due to two causes : in the first place, although it is more soluble in a dilute solution of salt than in fresh water, yet it reaches its maximum solubility at a density of 1.033, and after this point concentration of the saline solution diminishes the amount which can be held in solution, and the calcic sulphate is perfectly insoluble in a saturated brine. The second cause for its deposition is the rise in boiling point which accompanies the increase in density, the higher the temperature the less the solubility of the calcic sulphate becomes, so that when 284° to 302° F., or 140° to 150° C. is reached it becomes perfectly insoluble, both in sea and fresh water.

If sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1.09), to prevent the deposition of the calcic sulphate ; but any such regulation of the density is rendered abortive by the fact that pressure and consequent raising of the boiling point acts upon the calcic sulphate in solution in exactly the same way as concentration and increased temperature, so that in the older forms of boiler, working even at a comparatively low pressure, most of the sulphate was deposited, whilst in the high pressure boilers now in use, if the water contains the smallest trace of calcic sulphate, it will be deposited; and as any deposit formed amongst the tubes in such a boiler cannot easily be got at, it is practically impossible to use sea water in them, and they are supplied with the water from the condenser augmented by distilled water made in special distilling plant. The question has been raised as to whether, if sea water were mixed with distilled water so as to greatly reduce its density, it would deposit the calcic sulphate; but experiment shows that, even if sea water is mixed with many hundred times its bulk of distilled water, the minute trace present is deposited under pressure when the temperature approaches 284° F. or 140° C. So that when, through a breakdown in the distilling apparatus, sea water has to be used with the condenser water in even very small quantities, a slight scale is sure to be formed. When a saline solution containing calcic sulphate is heated under pressure or concentrated until calcic sulphate begins to separate, the sulphate will continue to precipitate even after the liquid has cooled down or the pressure has been removed; and, finally, when calcic sulphate has separated at a high temperature or pressure from sea water, even though the water has only the ordinary density (1.027), the rate at which the sulphate will redissolve is so extremely slow that its consideration may be neglected.

These two last properties are due to the form in which the calcic sulphate separates from sea water under pressure. Calcic sulphate occurs in Nature as gypsum, in which each molecule of calcic sulphate is combined with two molecules of water of crystallisation: when calcic sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcic sulphate to one of water;

vhilst, after deposition in the boiler and in contact with the ieated plates and tubes, it undergoes a further change of rystalline form, loses water, and becomes "anhydrite," vhich is pure calcic sulphate free from water of crystallisation, nd it is this change in crystalline form which binds deposits ontaining it into such a hard mass.

The presence of magnesic hydrate in boiler deposits has iven rise to many theories to account for its formation, that nost generally accepted being that it is due to the mutual lecomposition of water and magnesic chloride, which give ise to magnesic hydrate and hydrochloric acid, the action eing accelerated by the presence of metallic iron.

$$\begin{array}{ccccccc} \text{Iagnesic chloride} & & \text{Water} & & \text{Magnesic hydrate} & & \text{Hydrochloric acid} \\ MgCl_2 & + & 2(H_2O) & = & MgH_2O_2 & + & 2(HCl). \end{array}$$

When sea water is evaporated in contact with a large urface of metallic iron, no chloride can be detected in the iistillate until four-fifths of the solution has been distilled ver, whilst if the sea water be evaporated alone, it can be aken nearly to dryness without any decomposition. There s no doubt, however, that at a high temperature under ressure in marine boilers this decomposition takes place, but nly to a very small extent, a much large proportion of the nagnesic hydrate being formed by the decomposition of the nagnesic carbonate first deposited from the water in contact vith the heated tubes, and also by the action of magnesic hloride in the sea water upon the deposited calcic carbonate vhich mutually react upon each other, soluble calcic chloride nd magnesic oxide are formed, and the magnesic oxide inited with water forms magnesic hydrate, which is precipitated, carbon dioxide at the same time escaping.

This explains many points which the former theory leaves intouched—for instance, the fact of calcic carbonate being bsent from marine boiler deposit, or, if present, only in very small quantities; and also that chloride of iron is not found in the water of the boiler, which would be the case if any corrosion or pitting were due to the action of free hydrochloric acid.

In many analyses of boiler deposits no magnesic hydrate is returned, but considerable proportions of magnesic carbonate, which naturally would be formed by the magnesic hydrate absorbing carbon dioxide on exposure for any length of time to the air.

Sodic chloride, magnesic chloride, and sulphate are not found as usual constituents of boiler scale; but in cases of heavy incrustation, pockets are found in the deposit filled with microscopic crystals of these salts which have slowly filtered in solution into cavities in the incrustation, and have been deposited there on evaporation of the liquid.

An examination of the arrangement of the various portions of these deposits gives a fair idea of their formation. The crystalline crusts of calcic sulphate are always thickest and purest, and, for this reason, hardest in contact with the tubes or plates of the boilers where they have been most heated, but one also finds these layers throughout the deposit, in many cases having a nodular form; and this goes to prove that after the deposit has come down as a mud, the calcic sulphate being deposited already in small dense crystals, sinks through the ligher portions, and forms first a thin, and eventually a thick coating, which, by continuous heating under pressure changes its crystalline form, giving up moisture, and becomes "anhydrite," whilst the deposit above it gradually becomes thicker and thicker, and more crystallisation of the calcic sulphate takes place, pieces of mill scale and other foreign substances present in the mud forming nuclei round which the "anhydrite" crystallises; the lighter portions, consisting of magnesic hydrate and traces of calcic carbonate, settling into any spaces that remain, and completing the deposit.

When distilled water only is used, a slight coating is ormed, practically consisting only of organic matter, whilst at any time through a break-down in the distilling apparatus ea water is mixed with the distilled water, a thin and very ard scale of calcic sulphate is formed. An incrustation of is character gave on analysis :—

Calcic sulphate	90.84
Magnesic hydrate	.75
Sodic chloride	1.41
Silica	.85
Copper carbonate	1.11
Oxides of iron and alumina	.24
Organic matter	2.96
Moisture	1.84
	100.00

This scale is of great interest from the presence in it f the carbonate of copper. It is well known that distilled ater has a far greater solvent effect upon metals than a ater containing certain salts in solution, and it is quite coneivable that the distilled water from the surface condensers ttacks the brass and copper tubes and fittings, and deposits the opper on the tubes of the boiler, although in only small uantities; and it is interesting to note that the green spots ue to the presence of the copper are all on the under side of he scale, that is, in contact with the metal of the boiler ubes, showing that in all probability it had been deposited, s suggested, from the water in the boiler, and in contact ith the iron would set up local galvanic action and tend o produce pitting.

The loss of heat and waste of fuel entailed by the presence f boiler scale is enormous, and has been estimated by various observers at very different values. The latest estimates, however, go to show that $\frac{1}{6}$th of an inch of scale necessitates the use of 16 per cent more fuel, $\frac{1}{4}$th of an inch 50 per cent. and $\frac{1}{2}$ an inch 150 per cent. additional coal; the resulting waste of coal in the Service, however, being oftener laid to the credit of the state of the ship's bottom than to the condition of her boilers. Waste of fuel, however, is not the only drawback brought about by incrustation: the deposit being a bad conductor of heat, the tubes and plates of the boiler soon become overheated and burnt on the outside, whilst rapid corrosion is set up on the inner surface: iron at temperatures far below visible red heat, decomposing water and combining with the oxygen whilst hydrogen is liberated.

Even when calcic sulphate is not present, or is only present to a small extent, as in the deposits from fresh water, the tubes should be allowed to cool down before the boiler is blown off, as if this is not done, the loose soft deposit of calcic carbonate, when the water has all run off, bakes to a hard tough scale, which acts as a ground work for further deposits.

The importance of preventing boiler incrustation, and thereby avoiding the enormous waste of fuel and injury which it entails, has not been without its effect upon the minds of inventors, and almost every conceivable substance, from potato parings to complex chemical reagents, has from time to time been patented for this purpose, but they have all more or less failed for marine boilers, because either they have had an injurious effect upon the metal of the plates, or else have produced an enormous bulk of loose deposit, which although easily cleaned out if the various parts of the boiler were accessible, and if it were only being used intermittently, yet in a marine boiler continuously working, rapidly chokes the portions between the tubes, and brings about an even worse state of affairs than that originally existing.

For these reasons, no treatment of sea water in the boilers emselves is practically possible, and with high pressure bular marine boilers the water used must either be condenser ater made up to the required bulk with distilled water, as is present done, or else the condenser water must be augmented sea water especially prepared for the purpose in a separate pparatus before being supplied to the boilers; by heating the a water under pressure with sodic carbonate, and after pid filtration, supplying the water so treated to the feed ater tank or hot well.

If the engines of a vessel are in good condition, she will pproximately require 1 ton of water per 1,000 horse-power r 24 hours, to make up the volume of the condenser water the amount required for the boilers, so that even supposing e engines not to be in good order, and considerable waste to ke place, 20 tons per diem would be an outside allowance r even very large vessels.

In fresh water boilers incrustation can to a certain extent prevented, or at any rate diminished, by the addition of bstances which will prevent the calcic sulphate binding the lcic carbonate into a hard mass, and these so-called "anti-crustators" may be divided into two large classes: (1) Those nich have some definite chemical action, and (2) those nich are purely mechanical in their action.

Saline anti-incrustators. In this class sodic carbonate one form or another generally plays the principal rt. Its action is to convert the calcic sulphate and agnesic chloride into carbonate, and at the same time keep the water in an alkaline condition so as to prevent amage from acids.

lcic sulphate		Sodic carbonate		Calcic carbonate		Sodic sulphate.
$CaSO_4$	+	Na_2CO_3	=	$CaCO_3$	+	Na_2SO_4.

he hardening effect of the calcic sulphate being done away with, and the calcic carbonate precipitated in a soft condition, when it can be blown off.

Ammonic chloride is also used, and when boiled in presence of calcic carbonate decomposes it, forming soluble calcic chloride, whilst the ammonic carbonate volatilises.

Other alkalis and alkaline salts are also used, and even in some cases, acid mixtures, which latter, if they dissolve the scale, are fatal to the boiler plates.

Tribasic sodic phosphate and also sulphites have been used in some cases with fair results.

Vegetable and animal oils and fats should never be used, as not only do the fatty acids and salts attack the metal and increase corrosion, but the insoluble soaps formed by the combination of the fatty acids with the lime and magnesium salts in the water cling to the side of the boiler, and being broken up by the heat, yield a very tough form of scale.

Paraffin and its products. Paraffin oil causes the deposit to be thrown down in small rounded particles which can easily be got rid of by the blowcock. whilst it softens and breaks up previously formed scale ; indeed, the chief drawback to its use is that it so thoroughly cleans the joints of the plates that in many cases it causes them to leak. It should be first introduced when the boiler is empty, but afterwards can be added with the water—care must be taken that it is free from paraffin scale.

There are an enormous number of other organic compounds, proposed or in use, the action, if any, being mostly mechanical.

Zinc in metallic contact with the boiler plates in cases where sea water is used, acts beneficially in preventing corrosion of the plates but is of no use with fresh water, whilst other electrical and mechanical applications seem to have met with little or no success.

For land boilers where only hard water is to be obtained, it is better to soften the water by the Porter-Clark or other similar process, and to separate the precipitated lime salts by rapid filtration before supplying it to the boilers.

Feed water heaters act to a certain extent in softening the water supplied to a boiler and thus reducing incrustation; sometimes nearly 50 per cent. of the calcic carbonate contained by the water being deposited as mud in the heater.

CHAPTER VIII.

Carbon and some Compounds with Hydrogen.

Allotropic modifications of carbon—Diamond—Graphite—Carbon from organic sources—Absorbent properties of charcoal—General properties of carbon—Methane or marsh gas—Preparation and properties—Natural sources—Liberation of marsh gas in mines and coal bunkers—Fire damp—Safety lamps—Ethylene or olefiant gas—Preparation—Coal gas and its manufacture—Structure of flame—Burners for gas—Illuminating power of gas.

CARBON, next to oxygen, is perhaps the most widely distributed of the elements; it occurs in the free state as the diamond and as graphite, substances which although they are physically dissimilar, yet can be proved to be chemically identical, the dissimilarity of physical properties being probably due to some difference in the atomic arrangement.

Where an element occurs in forms which are physically dissimilar but chemically identical, the substances are called "Allotropic modifications," and the diamond and graphite are said to be allotropic modifications of the element carbon.

That they are both pure carbon is proved by the fact that when equal weights of the diamond and graphite are burnt in oxygen gas, in each case the same weight of carbon dioxide, and nothing else, is produced, whilst if a diamond be heated in the electric arc it swells up and is converted into a black mass resembling graphite.

The diamond occurs in well defined crystals and has a specific gravity of 3.5. It is one of the hardest substances known, and is used for cutting glass and polishing other precious stones. Graphite on the other hand is so soft that when drawn across a piece of paper some rubs off and leaves a mark, and on account of this property it is used as the core of pencils. It has a specific gravity of 2.2, and, unlike the diamond is a good conductor of electricity.

Charcoal and coke, obtained by heating organic substances out of contact with air, are often included as allotropic modifications of carbon, but they are not pure carbon, as they always contain oxygen, hydrogen, nitrogen. and any mineral constituents which may have been present in the original substance.

Bone black or animal charcoal, as we have seen, is a porous mass of calcic phosphate and carbonate containing carbon in a fine state of division, whilst lamp black is finely divided carbon and generally contains some oily matter and hydrogen.

The wonderful absorptive power for gases possessed by the porous forms of carbon obtained by heating bones and other animal and vegetable matter out of contact with air, has already been described, as well as its power of oxidising easily decomposable organic matter and gases, and also its efficiency in decolorising solutions.

The absorbent power of charcoal for gases varies (1) with the nature of the charcoal and (2) with the temperature; charcoal made from hard forms of woody fibre, such as the shell of the cocoanut having the greatest absorptive power, whilst the lower the temperature the more gas will be absorbed.

This power of absorption varies with different gases: at ordinary temperatures a cubic inch of freshly prepared cocoanut charcoal will absorb 170 cubic inches of ammonia gas, but only 17 of oxygen. The oxygen absorbed from the air by fresh charcoal is in a highly active condition, and for a certain space of time can be utilised for the destruction of oxidisable gases, but after being kept for a long time, the oxygen by contact with the carbon gradually becomes converted into carbon dioxide. Finely powdered charcoal sprinkled over decomposing animal matter absorbs the gases evolved, and oxidises them by virtue of the condensed oxygen in its pores, and for this reason it is largely used in the construction of sewer traps, and also in respirators.

ABSORPTION OF GASES BY CHARCOAL (HUNTER).[*]

1 *Volume of Charcoal at* 0°C. *and* 760 *mm. pressure, absorbs*—

Ammonia	171.7	volumes.
Cyanogen	107.5	,,
Nitrogen dioxide	86.3	,,
Ethylene	74.7	,,
Nitrogen monoxide	70.5	,,
Phosphuretted hydrogen ...	69.1	,,
Carbon dioxide	67.7	,,
Carbon monoxide	21.2	,,
Oxygen	17.9	,,
Nitrogen	15.2	,,
Hydrogen	4.4	,,

In Nature carbon is also found combined with hydrogen in coal, bitumen, shale, naphtha, the paraffins and numerous other hydrocarbons; with oxygen it is found as carbon dioxide which is present in the earth in enormous quantities, and which forms the large class of metallic salts called carbonates. In the vegetable kingdom the dry solids contain nearly 50 per cent. of it, whilst all animal matter is largely made up of it, fat containing as much as 79 per cent.

Phil. Mag. [4], xxix, 116.

Carbon is insoluble, non-volatile, and infusible at all ordinary temperatures, but signs of volatilisation are apparent in the electric arc. The diamond does not easily conduct heat or electricity, but the other forms of carbon are conductors.

Carbon forms an enormous number of compounds with hydrogen, two of great importance being methane or marsh gas (CH_4), and ethylene or olefiant gas (C_2H_4).

Methane, marsh gas or light carburetted hydrogen, is formed in Nature by the slow decay of vegetable matter out of direct contact with air; for instance, the vegetable deposits under water in marshes and pools give off this gas in abundance, and it is also one of the products of the conversion of woody fibre into coal.

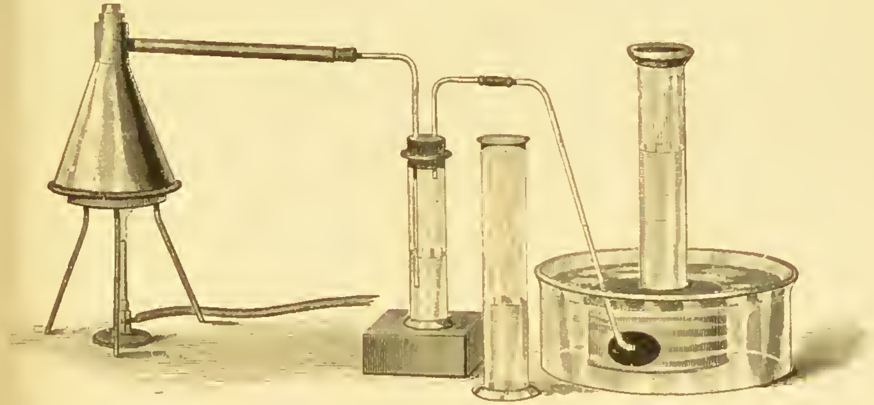

Fig. 27.

It is generally prepared for laboratory purposes by heating a mixture of sodic acetate and sodic hydrate, when:

$$\underset{\text{Sodic acetate}}{NaC_2H_3O_2} + \underset{\text{Sodic hydrate}}{NaHO} = \underset{\text{Sodic carbonate}}{Na_2CO_3} \quad \underset{\text{Marsh gas.}}{CH_4}.$$

The sodic hydrate is, in order to facilitate the operation, mixed with quicklime, which however takes no part in the decomposition. The heat required to effect decomposition is considerable, and it is therefore found necessary to conduct the operation in a metal generator (Fig 27); or, if a glass flask is to be used, to protect it by coating it with fire clay, otherwise it would soften at the temperature necessary to the evolution of the gas. Marsh gas is a colourless, odourless, tasteless gas, with no distinctive poisonous action.

It does not support combustion, but burns with a slightly luminous flame, forming carbon dioxide and water vapour. It is only slightly soluble in water, 100 volumes at 0°C. absorbing about 5.4 of the gas. Until lately it was supposed to be a permanent gas, *i.e.*, not reducible to the liquid state, but it has been liquefied by a combination of great pressure and cold.

Coal has the power of occluding marsh gas and again evolving it if the pressure be reduced or the temperature increased. This may occur in coal mines and also in the coal bunkers of a ship. In some cases 100 grains (6.48 grams) of coal will give off as much as 200 cubic centimeters of gas, which on analysis proves to be*

Marsh gas	89.61
Nitrogen	9.61
Carbon dioxide	0.23
Oxygen	0.55
	100.00

In the coal bunkers of a ship this liberation of the occluded gases will take place when a sudden fall in the barometer occurs, and also when the vessel passes into regions of increased temperature. And in order to prevent accumulation of the liberated gases the coal bunkers should be adequately ventilated, otherwise serious explosions may ensue, many vessels having been lost from this cause.

Marsh gas, when mixed with ten times its volume of air, or twice its volume of oxygen, forms a mixture which explodes with great violence on application of a light, forming carbon dioxide and water vapour :

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* Graham, *Phil. Mag.*

$$\begin{array}{ccccccc} \text{Marsh gas} & & \text{Oxygen} & & \text{Carbonic dioxide} & & \text{Water.} \\ CH_4 & + & 2O_2 & = & CO_2 & + & 2(H_2O), \end{array}$$

and in coal mines not only is marsh gas present occluded in the coal itself, and ready to issue into the workings when a fall of the barometer takes place, but also during the formation of coal under pressure great quantities of marsh gas are generated ; and this often is found accumulated under high pressure in the coal seams, discharging itself with considerable violence into the mines from the fissures made in hewing out the coal. The gas issuing from the fissure would burn quietly if a light were applied to it, since marsh gas is not explosive unless mixed with air ; but when the gas escapes into the mine and mixes with air it forms an explosive mixture as soon as the proportion of gas amounts to one eighteenth of the volume of the air, and the most explosive mixture consists of one volume of marsh gas and ten volumes of air. The explosive mixture of marsh gas and air is called fire-damp ; and the gases resulting from the explosion—carbon dioxide, water vapour, and nitrogen—are called choke-damp, and this often is as fatal in its effect as the explosion itself.

The mixture of oxygen and marsh gas requires a fixed temperature to ignite it, and unless this temperature be reached explosion cannot result. If a piece of wire gauze is held over a gas jet, the gas may be ignited above it without the flame passing through and igniting the gas on the underside ; the metallic wires composing the wire gauze conducting the heat away so rapidly that the temperature of the gas on the lower side does not rise to the point of ignition.

This simple principle was utilised by Sir Humphrey Davy in the construction of the safety lamp for miners. It consists of an oil lamp entirely surrounded with fine wire gauze, through which the air can enter and through which the products of combustion can pass out, but no flame can pass from the inside to the outside of the gauze, even if the explosive gases burn in the interior of the lamp.

In Fig. 28, three forms of safety lamps are shown; (1) is the old form first used and entirely surrounded with wire gauze, which, however, gave so feeble an illumination that the wire gauze immediately surrounding the flame was replaced by a glass cylinder (No 2), and until 1887 this was the best form in use; it has been shown, however, that although the flame, when burning under ordinary conditions cannot pass through the gauze, yet, a sudden disturbance of the air, such as is caused by the blasting of coal in the mine, will sometimes jerk the flame by a sudden impulse through the gauze, and so communicate with the explosive mixture outside, and to do away with this risk, a new form of lamp is being introduced in which the wire gauze cylinder is entirely surrounded by a shield of iron plate (No 3), which prevents the direct impact of the air upon the gauze, and greatly increases the value of the lamp.

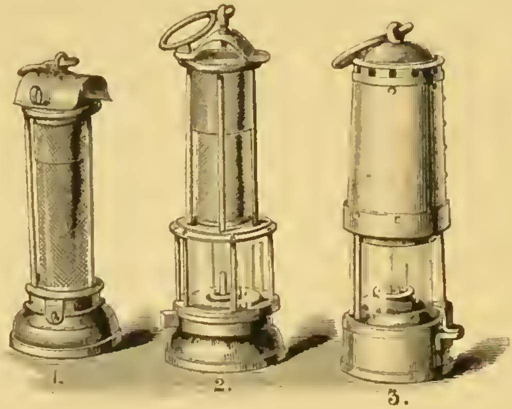

Fig. 28.

It would greatly decrease the risk of explosion in coal bunkers and in coaling vessels, if when a light is required, only such lamps were used, and employment of a naked flame never allowed, as besides the gas present, it has been shown that the presence of fine dust of coal in the air of the bunkers very much increases the liability to explosion. When methane or marsh gas is passed through a tube heated to bright redness it can eventually be decomposed entirely into carbon, which is deposited and hydrogen which passes on, the same decomposition taking place when a series of electric sparks is passed through the gas, and the hydrogen liberated occupies double the volume of the marsh gas decomposed :

$$\underset{\text{2 vols.}}{CH_4} = C + \underset{\text{4 vols.}}{2H_2}.$$

On analysis it is found to contain—

Carbon	75·0
Hydrogen	25·0
	100.0

from which the molecular formula (CH_4) is obtained; its molecular weight is $(12 + 4) = 16$ and density $\frac{16}{2} = 8$.

Ethylene or olefiant gas (C_2H_4) exists in small quantities in the gases evolved during the dry distillation of many organic bodies. It is prepared by acting upon alcohol with sulphuric acid, when the alcohol is dehydrated and olefiant gas liberated.

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sulphuric acid and water}}{H_2O,H_2SO_4} + \underset{\text{Olefiant gas.}}{C_2H_4}.$$

In preparing the gas 1 volume of alcohol and 4 volumes of strong sulphuric acid are mixed with sand, to prevent frothing, and are then heated, care being taken to avoid too high a temperature, which would cause the evolution of sulphur dioxide.

Ethylene or olefiant gas consists of 2 atoms of carbon combined with 4 of hydrogen; it is a colourless gas with a slightly sweetish taste; it can be condensed to a liquid by pressure at a temperature of—100° and burns in air with a luminous smoky flame. It is an important constituent of coal gas, which owes most of its illuminative power to its presence. When mixed with three times its own volume of oxygen it forms a highly explosive mixture, which if ignited combines forming carbon dioxide and water.

$$\underset{\text{Olefiant gas}}{C_2H_4} + \underset{\text{Oxygen}}{3(O_2)} = \underset{\text{Carbon dioxide}}{2(CO_2)} + \underset{\text{Water.}}{2(H_2O).}$$

It is called olefiant gas because when mixed with its own volume of chlorine it forms an oily liquid.

Like marsh gas it can be decomposed by passing a series of electric sparks through it, and also by heat, which breaks it up in three stages, dependant upon the temperature employed. Its percentage composition is

Carbon	85.7
Hydrogen	14.3
	100.0

Which gives the formula C_2H_4. Its molecular weight $=(24+4)=28$, and density $\frac{28}{2}=14$.

Coal gas, our most important illuminant, is produced by the destructive distillation of coal. The coal is heated out of contact with air in large retorts, coke remains behind in the retort, whilst the gaseous and liquid products distil over. The liquids, consisting of tar, ammoniacal liquor, &c., are condensed and collected in tanks; whilst the gases, after being purified are collected for use.

Cannel, or other bituminous coal rich in hydrogen, is heated out of contact with air in elliptical retorts, and the products of distillation are then led off by an ascending tube from the mouth of the retort. This tube, after ascending above the level of the bench of retorts, bends over and descends into a cylindrical tube, which is about half full of tar; and into this the delivery tube from the retort just dips, the tar closing the mouth of it gas-tight. This main collecting tube runs horizontally over the whole of the front of the bench of retorts, and they all discharge into it by means of their delivery tubes, each of which is sealed off by the tar, kept at a constant level by means of an overflow siphon at the end of the collecting tube, which is called the hydraulic main.

Each retort is fitted at the end which projects from the furnace with a mouth-piece and lid, which can be removed to allow of the coke being withdrawn and the fresh charge of coal inserted, and the vertical pipes which lead up to the hydraulic main, start from the top of the mouth-piece. The reason why these pipes are sealed by dipping under the surface of the liquid in the hydraulic main is, that in case one of the retorts should crack, the gas from the other retorts cannot escape down the pipe as would be the case if they simply opened into the main. A large quantity of volatile products make their way as vapour with the gas into the hydraulic main, where much condenses as tarry products and ammoniacal liquor (consisting of ammonia, carbonate and sulphide of ammonium, etc., in solution), and these run off through the overflow siphon to the tar well, where they are collected. The gas passes down from the hydraulic main to the atmospheric condensers, a series of tubes placed vertically, which are exposed to air, which cools down the gas as t passes through them and causes a further deposition of tar, ammoniacal liquor, and any easily condensable hydrocarbon which may be present. There is also generally an arrangement for artificially cooling the condensers in hot weather by means of water. After leaving the condensers the gas next passes through the scrubbers, which consist of towers built of iron plate and filled with coke, over which water or diluted ammoniacal liquor is sprayed and trickles down, meeting the gas which is made to pass up them. The alkaline liquor absorbs some of the sulphuretted hydrogen and carbon disulphide present in the gas, and also removes the last traces of tar and ammonia, and the gas still containing some sulphuretted hydrogen, carbon disulphide and carbon dioxide, passes on to the purifier.

It is important to get rid of these gases, as carbon dioxide when present even in small quantities affects the illuminating power of the gas to a serious extent, whilst carbon disulphide and sulphuretted hydrogen on combustion produce sulphur dioxide, which in contact with air and moisture becomes oxidised to sulphuric acid, and this has a very detrimental effect upon the furniture and drapery of rooms.

The gas first comes to the dry lime purifiers, where it passes over trays or through grids, on which is placed slaked lime, and this absorbs the carbon dioxide and a good deal of sulphuretted hydrogen and carbon disulphide, forming calcic carbonate and sulphide, whilst cyanides are also found in the spent lime. To remove the last of the impurities the gas is now passed through other purifiers containing hydrated ferric oxide or else a mixture of sulphate of iron, sawdust and slaked lime, which combining with the impurities keeps them back, whilst the gas passes on to the gasometer and thence to the mains.

The coal gas, as it leaves the works, is a mechanical mixture of hydrocarbons diluted with hydrogen, and the following analysis gives a good general idea of its composition, which, however, differs very widely with the kind of coal used, and the temperature at which the retorts are fired.

Gas from Cannel Coal.

Hydrogen	45.841
Marsh gas	40.954
Olefiant gas	5.504
Carbon monoxide	4.167
Carbon dioxide	1.950
Nitrogen	1.445
Oxygen	0.139
	100.000

and the gas owes its illuminating power to the olefiant and marsh gases, and any other hydrocarbons which may be present. Of late years the gas industry has received a considerable impetus, the secondary products obtained from tar being employed for the production of the beautiful coal tar colours.

Coal tar consists of the following substances:—

Benzol	1.5
Naphtha	35.0
Naphthaline	22.0
Anthracene	1.0
Carbolic acid	9.0
Pitch	31.5
	100.0

and if this tar be carefully redistilled, we find that it can be separated into various constituents which distil over at different temperatures.

First, light oils pass over, from which benzol and its homologues can be obtained; then heavy tar oil, from which carbolic acid is made, and pitch is left, from which a substance called anthracene can be separated.

The benzol or benzene obtained is the source from which aniline is prepared, and it is from aniline that most of the coal tar colours are obtained.

When benzol is acted upon with fuming nitric acid, nitro-benzol is formed, and on treating this nitro-benzol with dilute sulphuric acid and zinc dust, or acetic acid and iron filings, hydrogen is evolved and in its nascent state attacks the nitro-benzol and removes its oxygen, leaving behind the compound of carbon, hydrogen and nitrogen, called aniline; and it is from aniline that the brilliant colours, mauve, magenta, and other purples and reds are obtained by acting upon it with oxidising agents, and from it can also be obtained the beautiful series of aniline yellows, blues and violet.

The use of coal gas for illuminating and heating purposes necessitates the consideration of the structure and properties of flame.

On examining an ordinary flame such as that of a candle, it is seen to consist of three concentric zones—the innermost (A, Fig 29) around the wick, appearing almost black, the next (B), emitting a bright white light, and the outermost (C), being so pale as to be scarcely visible in broad daylight. The dark innermost zone consists merely of the gas generated from the wax of the candle, to which the air does not penetrate, and which is therefore not in a state of combustion. In the second or luminous zone combustion is taking place, but is not perfect, a quantity of carbon separating unburnt, which being heated to incandescence renders the flame luminous and the pale outermost zone where the flame, being in contact with the air, combustion is perfect, and all the carbon is burnt to carbon dioxide.

In order that a flame may emit a brilliant light, it is necessary for it to contain either particles of solid matter which can be heated to incandescence, or else for the gases to be under such pressure that they cannot expand greatly when burning.

Phosphorus burns with a luminous flame, because the product of combustion is a white powder which renders the came luminous; but hydrogen burns in oxygen with a non-luminous flame unless subjected to great pressure, which prevents the expansion of the aqueous vapour formed by the combustion, and renders the flame luminous.

Non-luminous flames can be rendered luminous by introducing solid particles into them.

Candles are made of various kinds of volatile fats and waxes, all of which contain carbon and hydrogen. The commonest kinds are made from the tallow obtained from the

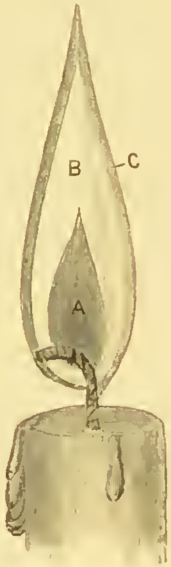

Fig. 29.

fat of oxen and sheep, whilst the better kinds are made from wax, paraffin, palmitin, and spermaceti. When a candle is lighted, the ignited wick melts the wax in its immediate neighbourhood, and by capillary attraction sucks it up: the heat then partially decomposes and converts it into vapour, and the burning vapour forms the flame of the candle. The oils used for illuminating purposes have very much the same composition, consisting almost entirely of carbon and hydrogen; and when these are burnt in lamps, they, like the candle wax, are drawn up to the flame by the capillary attraction of the wick, and are there decomposed into olefiant gas, marsh gas, acetylene, &c., which maintain the flame, these being the same gases which give the illuminating power to a gas flame.

If an ordinary gas flame is examined, these zones can be easily perceived, and if air be supplied to the interior of a flame it loses its luminosity, an effect partly due to the oxygen so supplied causing complete combustion of the carbon, and partly also to the diluting influence of the other constituent of air, nitrogen.

It is upon this principle that the Bunsen burner is constructed.

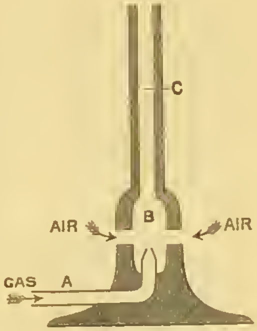

Fig. 30.

Gas is brought through the tube (A, Fig. 30) under the ordinary pressure, and is discharged from a small orifice into a metal chamber, which has holes at the side open to the air, and into which is screwed a vertical tube (C) which is immediately over the orifice from which the gas is issuing. The gas rushes upwards and impinges on the sides of the tube (C), diminishing the pressure at the sides of the chamber (B) by its uprush, and so air is drawn in through the holes at the side, the mixture of air and gas passing together up the tube and being burnt at the top. That the non-luminosity of the flame is due to the air introduced can be proved by closing the air holes with the fingers, when the ordinary luminous gas flame is at once obtained. The Bunsen flame is smaller and more compact than the flame given by the same amount of gas burning without admixture of air, and for this reason is hotter, but it must be remembered that unless some of the constituents of the gas finally escape complete combustion, the total quantity of heat generated by equal quantities of gas will be the same, whether it affords a luminous or non-luminous flame; indeed, in the Bunsen flame the nitrogen introduced being incombustible would tend to lower the temperature.

In the Bunsen flame, and also in a blowpipe flame obtained by blowing air through an ordinary flame, the different parts have different chemical functions.

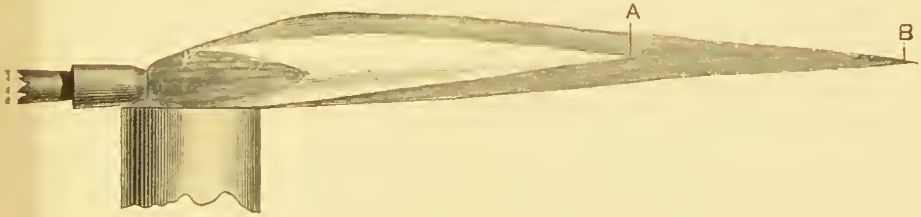

Fig. 31.

If a piece of metallic copper be held just beyond the extreme tip of the flame (B, Fig. 29), it will quickly become coated with black copper oxide, because the flame will have used up all the oxygen it requires for its own combustion, and the great heat generated will make any oxidisable metal combine with the oxygen of the air present, and for this reason the outer is called the oxidising flame. If, however, the copper oxide so formed is held in the inner zone of the flame at (A, Fig. 31), there combustion is not complete, and the hot carbon or carbon monoxide will attack the metallic oxide and take from it its oxygen, forming carbon dioxide, at the same time reducing the copper oxide to metallic copper; hence the inner zone is called the reducing flame.

In the complete combustion of any of the hydrocarbons, carbon dioxide and water vapour are the products formed.

When coal gas is burned for the production of light, in order to obtain the maximum illuminating power, the first requisite is to have as high a temperature as possible, and to obtain this the top of the burner must be of a non-conducting substance such as steatite; next, the gas must be supplied to the burner in a steady flow and the flame must be supplied with an even flow of air. Of ordinary gas burners there are two forms, those giving a flat flame such as the batswing and fishtail burners, and the Argand burners in which the burner is ring shaped, forming a hollow cylinder of flame, acted upon by the air from both inside and outside; with this burner a chimney is needed to increase the draught and throw the air with sufficient force against the flame. The regulation of the air supply to a flame is a matter of great importance, as too great a supply of air decreases the illuminating power of the flame by effecting a too rapid combustion of the carbon, and thus prevents it giving out the maximum amount of light; whilst too small a supply allows some of the carbon to escape unburnt, and gives rise to a smoky flame.

Of late years, the importance of raising the temperature of the flame to as high a degree as possible has been fully recognised, and the gain in illuminating power per foot of gas burnt is very great, and it is upon this principle that most of the new burners are being constructed.

This may be accomplished in two ways—*First*, by having more than one flame in the gas lamp and causing them nearly to touch, when it is found that two burning together give a light considerably more intense than could be obtained if they were burning apart, and this is caused by the augmentation of the heat of each individual flame by heat radiated from the other, and also by the heating of the air sucked up between the flames; on this principle the big cluster burners are made; and *secondly*, we have what are called regenerative burners, in which the heat from the flame and the hot products of combustion are made to heat the gas and air before they enter into combustion. Of late years two incandescent gas lamps have attracted some attention, the principle being to supply sufficient air to a gas flame to burn up all the carbon and to give a non-luminous but very hot flame, in which certain non-combustible bodies are heated to incandescence and emit light. The Lewis lamp consists of a small burner of this type, in which a cone of platinum wire gauze is heated; and the Welsbach light is on the same principle, the platinum gauze cone being replaced by a hollow cone of filaments of the oxides of some of the rarer metals, and these being heated to bright whiteness give out a very pure white light.

The illuminating power of lamps and gas flames is always now compared with the light emitted by a spermaceti candle burning 120 grains per hour; and the relations between the lights are determined by means of an apparatus called a photometer.

When light diverges from a luminous source, its intensity diminishes as the square of the distance increases: so if we arrange two lights, one the standard candle, and the other the light to be tested, at such distances from a fixed object that the light thrown upon it from each source of light is equal, the relative intensities of the two lights can be found by squaring the distance of each light from the object.

Selecting the best burner of each class for photometric comparison and experiment, and using coal gas of the quality supplied to London, the following results have been arrived at:

Name of burner	Illuminating power in candles per cubic foot of gas consumed
Batswing	2.9
Argand	3.3
Incandescent	6.0
Regenerative	10.0

CHAPTER IX.

THE OXIDES OF CARBON.

Carbon dioxide—Preparation and properties—Solubility—Aërated waters—Liquefaction of carbon dioxide—Critical temperature—Composition of carbon dioxide—Carbon monoxide—Preparation and properties.

CARBON, when burnt in a free supply of air or in oxygen, forms carbon dioxide (CO_2), unless the combustion be checked or a large excess of red hot carbon be present, in which case a second oxide—carbon monoxide (CO) is formed.

Carbon dioxide (CO_2) occurs free in the air and is also present in many mineral waters, and is frequently found in wells and old mine shafts often proving fatal to workmen who descend them without first taking the precaution of ascertaining its absence.

Carbon dioxide is found combined with various bases as carbonates, which are very plentiful in Nature, whole chains of hills being formed of calcic carbonate or chalk.

The most convenient way of preparing it is to act upon calcic carbonate with a strong acid, which expels the carbon dioxide and unites with the calcium, at the same time forming water.

$$\overset{\text{Calcic carbonate}}{CaCO_3} + \overset{\text{Hydrochloric acid}}{2(HCl)} = \overset{\text{Calcic chloride}}{CaCl_2} + \overset{\text{Water}}{H_2O} + \overset{\text{Carbon dioxide.}}{CO_2}.$$

This is most conveniently done by taking a dense form of calcic carbonate, either limestone or marble (which, as well as chalk, are all calcic carbonate but formed under different circumstances) in order to avoid frothing which would follow if the less dense substance (chalk) had been used, and after breaking into small pieces, placing it in the two-necked bottle (A, Fig. 32), the calcic carbonate is now covered with water and hydrochloric acid is poured down the thistle funnel (B); carbon dioxide escapes in abundance and is conducted by the leading tube (C) under water in the pneumatic trough (D), where it can be collected by displacement of water. Carbon dioxide is a colourless, odourless gas which will not burn or support ordinary combustion; it has a slight acid taste and reaction.

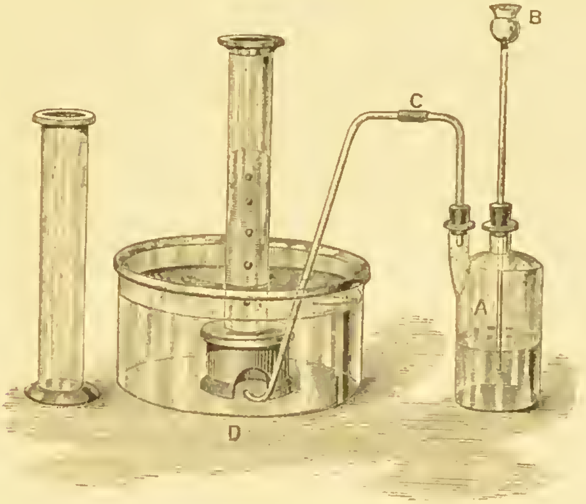

Fig 32.

Nearly all spring waters contain the gas carbon dioxide dissolved in them in greater or less quantity; and many of the properties of spring water, such as temporary hardness, are due to its presence, the carbon dioxide in solution forming an unstable acid called carbonic acid, which is able to dissolve many substances, such as chalk (calcic carbonate), magnesic carbonate, and ferrous carbonate, which the water alone is unable to do, or at any rate only to a small extent. The carbon dioxide so present is obtained by the water partly from the subsoil through which it has filtered, and to a much larger extent from subterranean sources. It is well known that caverns, deep wells, mines, &c., nearly always contain large quantities of this gas, and also that it issues in enormous quantities from fissures in the ground in various parts of the globe; and as it is always present in underground strata, it is evident that water permeating these strata will become charged with as much of this gas as it can take up.

Water, under ordinary conditions of temperature and pressure, dissolves its own volume of the gas—that is to say, at 15° C., and with the barometer standing at 30 inches (760 mm.) a pint of water will dissolve a pint of the gas; but a change either in the temperature of the water or in the pressure of the atmosphere, will be accompanied by a change in the quantity of gas dissolved, so that if the water were cooled down to 0° C., the pint of water, instead of dissolving 1 pint of the gas, would dissolve nearly $1\frac{3}{4}$ pints, and any increase of the atmospheric pressure, shown by a rise in the barometer, would also cause an increased absorption of the gas, and if the water be then brought to its initial temperature of 15° C., or if the extra pressure were removed from its surface, the amount of carbonic acid over and above the pint it can dissolve under those conditions once more escapes and causes the water to effervesce.

In the case of many springs which rise from considerable depths, the water has come in contact with carbon dioxide under considerable pressure, the gas being confined in subterranean caverns through which the water passes; and such springs, on reaching the outer air, give off once more the excess of gas, which they have taken up, the pressure being reduced to ordinary atmospheric pressure. Such waters sparkle and effervesce, and being very pleasant to the palate were much sought after as table waters; but, from the rarity of the springs and the paucity of the supply, waters of this kind, such as the natural seltzer water, commanded a high price, and attempts were made to manufacture them artificially.

The machines in use for saturating water with carbon dioxide are numerous, but the principle in nearly all is the same. (Fig. 33.)

Carbon dioxide is generated by acting upon some carbonate, generally carbonate of lime in the form of whiting, with dilute sulphuric acid, and the gas so generated is led into a gasometer, after having been washed by passing through water; the gasometer is connected with a gunmetal pump, which also is connected with a reservoir containing pure water, in which about one ounce of bicarbonate of soda has been dissolved to every gallon of water; this solution and the carbon dioxide are forced together by means of a pump into a very strong condenser lined with tin, and in which the gas and liquid are agitated together by means of revolving arms fixed on a spindle and driven at high speed, and it is in this condenser that the water becomes highly impregnated with the gas under pressure.

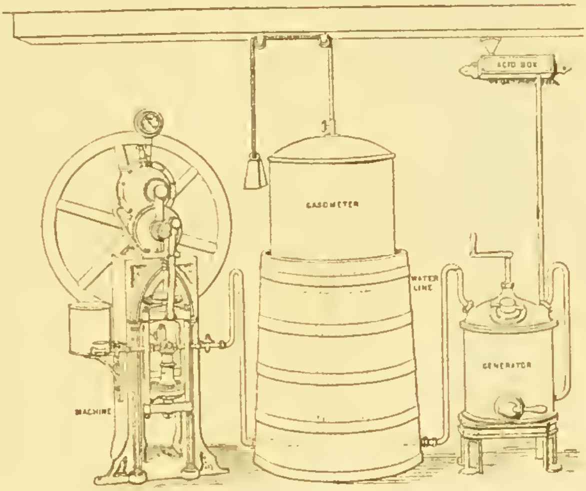

Fig. 33.

The liquid is then drawn off, corked and wired down whilst still under pressure, and so long as the cork fits airtight into the bottle the pressure will be maintained, but the moment the cork is taken out the liquid is brought back to ordinary atmospheric pressure, and the excess of gas escapes.

The main points to be attended to in making a highly aërated water are, to drive all air out of the apparatus before the manufacture commences, and to maintain a regular, but not too high pressure in the condenser chamber.

The earliest forms of aërated waters were made by mixing together in the bottle two solutions which would act upon each other and generate carbon dioxide in the liquid itself; the great drawback to this being that the salts so introduced have an effect upon the system, which, except in special cases, it is well to avoid.

In sparkling wines and the old-fashioned ginger beer, carbon dioxide is generated in the bottle by fermentation of the liquid present, and this gas as it escapes into the space above the liquid creates a greater and greater pressure, and assists its own solution.

In the various forms of gasogenes used for making effervescing drinks in the house, a mixture (usually consisting of tartaric acid and bicarbonate of soda) is introduced into the lower portion of a glass apparatus, and generates carbon dioxide, which passing up through a tube develops pressure, and saturates water in the upper part of the arrangement.

Carbon dioxide can be condensed to a liquid by cold or by a pressure of 36 atmospheres, and if the liquid carbon dioxide is allowed to assume the gaseous state, by letting some of the liquid escape into the air, the cold produced by the sudden transition from the liquid to the gas is so intense that some of the liquid is frozen into the solid form, and produces a snow like substance which blisters the hands when pressed upon the skin and has a temperature below $-78°$ C.

To produce the solid carbon dioxide, the gas is first liquefied by pressure in an iron cylinder (Fig. 34), and then by opening a valve the liquid carbon dioxide by its own pressure is driven up a tube which goes to the bottom of the cylinder and escapes into a brass box; here under ordinary atmospheric pressure the liquid rapidly assumes the gaseous state, and abstracts heat from the surrounding objects, and so reduces the temperature that it freezes to a solid, the gas escaping through the wooden handles of the box which are hollow; on opening the box the solid carbon dioxide is found as a white substance like snow, and if some of this be placed on mercury and a little ether added, so intense a degree of cold will be produced that the mercury is frozen to a solid. By mixing this solid carbon dioxide with ether a temperature of – 101 degrees can be obtained. If carbon dioxide be compressed at a temperature of 32° C. it refuses to liquefy even under a pressure of 109 atmospheres (109 × 15 lb. on the square inch), but on cooling the compressed gas it is suddenly converted into a liquid.

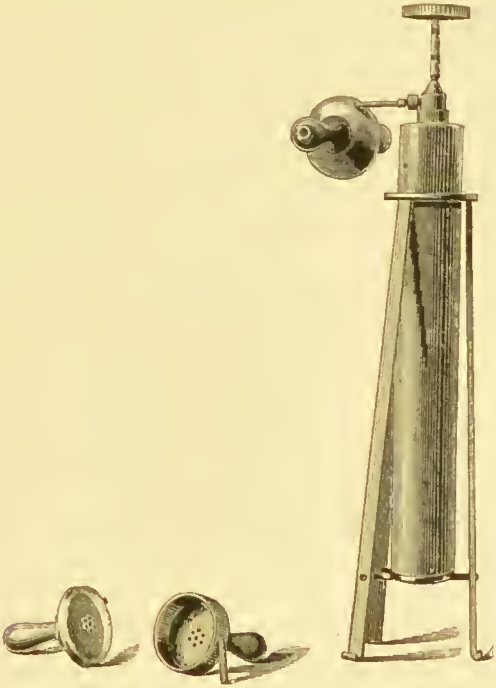

Fig. 34.

The same phenomenon is observed with all gases when attempting to liquefy them by pressure—that is to say there is a temperature at or above which no pressure will cause them to liquefy. This point is called the critical point, and varies with the nature of the gas.* Carbon dioxide is 22 times as heavy as hydrogen, and may be poured from one vessel to another like water. It does not burn or support combustion in the ordinary sense of the word, but the metal potassium will burn in it, decomposing it, and forming potassic oxide at the same time depositing carbon.

In most of its properties it resembles nitrogen, but can be distinguished from it by giving a white precipitate with lime water, with which it combines, forming calcic carbonate, and as this is practically insoluble, it is thrown down as a precipitate.

$$\overset{\text{Lime water or calcic hydrate}}{CaH_2O_2} + \overset{\text{Carbon dioxide}}{CO_2} = \overset{\text{White precipitate of calcic carbonate}}{CaCO_3} + \overset{\text{Water.}}{H_2O}.$$

Carbon dioxide is completely absorbed by sodic or potassic hydrate, whether in solution or when the solid is moistened. The carbon dioxide unites with the alkaline hydrate forming a carbonate and liberating water,

$$\overset{\text{Potassic hydrate}}{2(KHO)} + \overset{\text{Carbon dioxide}}{CO_2} = \overset{\text{Potassic carbonate.}}{K_2CO_3} + \overset{\text{Water.}}{H_2O},$$

a reaction frequently used to separate carbon dioxide from other gases not absorbed by the alkaline hydrate.

Carbon dioxide in presence of water or moisture has faint acid properties, but does not completely neutralise the alkalis, and when added to a solution of blue litmus turns it claret red; but the original blue colour can be restored by boiling which drives off the carbon dioxide; other acids, like sulphuric or nitric, give with blue litmus a bright red, which is permanent on boiling.

The solution of carbon dioxide in water is supposed to contain the hydrogen salt H_2CO_3, carbonic acid, from hich the class of salts called carbonates is produced by placement of the hydrogen by metals, but the acid has never een isolated.

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* Andrews.

It forms two classes of salts—normal carbonates, in which oth atoms of hydrogen are replaced by metals, as :

Sodic hydrate Carbonic acid Sodic carbonate Water.

$$2(NaHO) + H_2CO_3 = Na_2CO_3 + 2(H_2O);$$

d acid carbonates, or bicarbonates as they are often called, which only half the hydrogen present is replaced :

Sodic hydrate Carbonic acid Sodic bicarbonate Water.

$$NaHO + H_2CO_3 = NaHCO_3 + H_2O.$$

arbon dioxide can be proved to contain carbon by passing

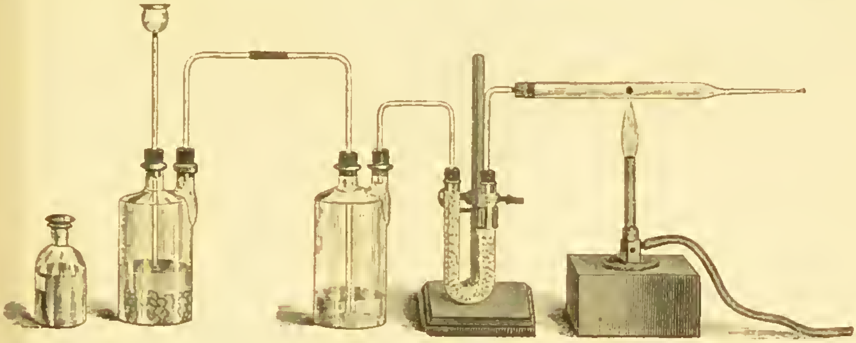

Fig. 35.

e well dried gas over a piece of the metal potassium heated the melting point in a thin glass tube (Fig. 35).

The carbon dioxide is generated from marble and hydro-loric acid and is then passed through a wash bottle and calcic chloride tube in order to dry it. The potassium is aced in a drawn out test tube, and heated by a Bunsen me, when it burns with a red glow, at the expense of the ygen contained in the carbon dioxide, and deposits carbon a black mass.

Carbon dioxide Potassium Potassic oxide Carbon.

$$CO_2 + 4K = 2(K_2O) + C,$$

d the potassic oxide so formed at once combines with the excess of carbon dioxide present, forming potassic carbonate.

Potassic oxide		Carbon dioxide		Potassic carbonate.
K_2O	$+$	CO_2	$=$	K_2CO_3.

Carbon dioxide on analysis has the percentage composition :—

Carbon	$27{\cdot}\dot{2}\dot{7}$
Oxygen	$72{\cdot}\dot{7}\dot{2}$
	$99{\cdot}\dot{9}\dot{9}$

and on dividing the percentage composition by the atomic

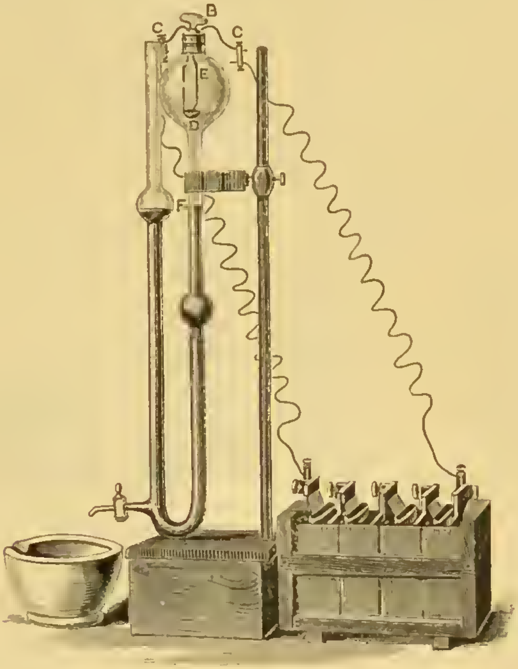

Fig. 36.

weights of the elements they represent, we obtain quotient standing to each other in the ratio of one to two, hence w deduce the formula CO_2 for the gas.

When carbon is burnt in oxygen gas, the oxygen is con verted into carbon dioxide, which occupies the same volum as the oxygen used in its formation :—

Carbon		Oxygen, 2 vols.		Carbon dioxide 2 vols.
C	$+$	O_2	$=$	CO_2.

This may be shown by burning carbon in oxygen confined er mercury in the apparatus. (Fig. 36.)

A bulb tube is closed by a glass stopper (B), through ich pass a small deflagrating spoon (D) and a thick copper re (E); these are joined by a piece of thin platinum wire, ich is coiled round a small lump of charcoal in the spoon). The bulb having been filled with oxygen, the opper is closed and the height of the mercury at (F) having en noted, a current from a battery is passed through the nnections (C C), and heats the thin platinum wire to redness, iting the charcoal, which burns in the oxygen, forming rbon dioxide. The heat generated by the combustion pands the gas and depresses the mercury, but on allowing e gas and apparatus to cool down to its original mperature, the mercury again rises to the point (F), owing that no change in volume has taken place.

The molecular weight of carbon dioxide is

$$12 + 2(16) = 44, \text{ and its density is } \frac{44}{2} = 22.$$

Carbon monoxide (CO) is a colourless, tasteless gas, ghly poisonous and very little soluble in water; it does not pport combustion but burns with a pale blue flame, taking another atom of oxygen and becoming carbon dioxide. may be prepared by acting upon oxalic acid with sulphuric id, oxalic acid consisting of hydrogen, carbon and oxygen in e proportions necessary to form water, carbon dioxide, and rbon monoxide. When this is heated with sulphuric acid, e elements of water are taken up by the sulphate, and rbonic dioxide and monoxide are set free; these mixed ses are now led through sodic hydrate, which absorbs the rbon dioxide, forming sodic carbonate and water, and the rbon monoxide passes on free.

This operation is carried on in an apparatus such as is own at Fig. 37.

The mixture of oxalic and sulphuric acids is heated in the flask (A, Fig. 37), fitted with a safety funnel (B) and the mixed carbon monoxide and dioxide pass by means of the leading tube (C) through a solution of sodic hydrate in the wash bottles (D D); this absorbs some of the carbon dioxide, the remainder being got rid of in the absorption tower (E), which is filled with glass marbles, on the top of which are sticks of moistened sodic hydrate; the purified carbon monoxide then passes on and is collected over water in the pneumatic trough (F). The action may be represented by the equations:

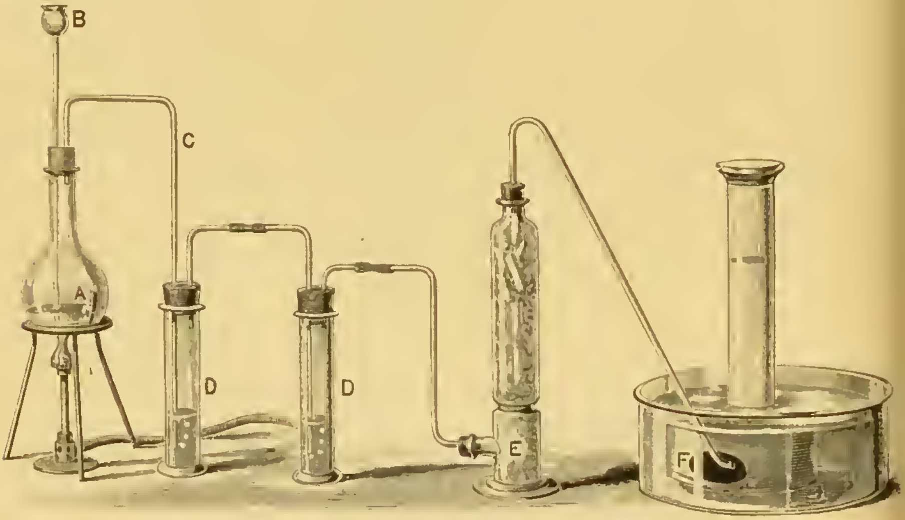

Fig. 37.

$$\overset{\text{Oxalic acid}}{H_2C_2O_4} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Dilute sulphuric acid}}{H_2SO_4,H_2O} + \overset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2} + \overset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO.}$$

and

$$\overset{\substack{\text{Carbon}\\\text{monoxide}}}{CO} + \overset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2} + \overset{\substack{\text{Sodic}\\\text{hydrate}}}{2(NaHO)} = \overset{\substack{\text{Sodic}\\\text{carbonate}}}{Na_2CO_3} + \overset{\text{Water}}{H_2O} + \overset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO.}$$

When carbon dioxide is passed over red hot charcoal, the dioxide gives up one half its oxygen to the carbon, and forms twice its own volume of carbon monoxide.

Carbon dioxide, 2 vols.		Carbon.		Carbon monoxide, 4 vols.
CO_2	$+$	C	$=$	$2(CO)$.

The blue flame of carbon monoxide may often be seen at e top of a clear coke fire, and its formation may be explained the following way: At the bottom of the fire the fuel is in ntact with excess of air drawn through it by the up-draught the chimney, and here the fuel burns to water and carbon oxide; carbon dioxide passing up through the red hot ke, becomes reduced to carbon monoxide, and this in time oming in contact with more air at the top of the fire, burns ith its characteristic pale blue flame, again forming carbon oxide, which, with the water vapour, and nitrogen of the air, ass up the chimney.

Carbon monoxide has a powerful reducing action, and will ke oxygen from several of the metallic oxides, under the fluence of heat, forming carbon dioxide, and leaving the etal free, an action which is utilised in metallurgical ocesses.

The gas has such powerful poisonous properties, that one er cent. of it in air renders the air perfectly unfit to breathe,* nd many fatal accidents have arisen from its being formed uring checked combustion, as when metallic surfaces cooled n one side by water are exposed to a gas flame, as is found n some forms of "water heaters"; also by the imperfect comustion taking place in kilns, in slow combustion stoves, and n charcoal pans.

It may be distinguished from carbon dioxide by burning ith a blue flame, and not affecting lime water until comustion has converted it into carbon dioxide.

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* Leblanc.

CHAPTER X.

FUEL.

Woody fibre—Wood as a fuel—Circumstances affecting its value—Moisture in wood—Wood charcoal—Peat—Coal—Formation of coal—Effect of hydrogen on combustibility—Composition of coal—Kind of coal required for the Navy—Stowage—Heating of coal—Ash—Coke—Liquid fuels—Russian and American petroleum—Heavy tar oil—Dead oil—Injectors for liquid fuel—Gaseous fuels—Coal gas—Water gas—Generator gas—Calculation of calorific value of fuels—Evaporative power of fuel—Determination of the thermal value of fuels—Calorific intensity.

In order that any substance should take rank as a fuel it must be of such universal occurrence as to be easily obtainable in all inhabited countries, and this restriction has practically reduced our common fuels to wood and the substances which have been derived from it by either natural or artificial processes. Woody fibre or cellulose forms the basis of all vegetable solids, and on analysis it has the percentage composition :—

Carbon	44·44
Hydrogen	6.17
Oxygen	49·39
	100.00

which gives us the formula $C_6H_{10}O_5$. In wood, the main constituent cellulose, is common to all species, the chief differences being in the density and constituents of the sap.

As a fuel the value of wood varies with the amount of moisture it contains and the ash, which is made up chiefly of the mineral constituents of the sap.

The moisture in wood varies with many circumstances, such as the season of the year at which it was cut down, the species of tree and the way in which it has been kept between the time of cutting and burning. When wood is cut in the spring, say during April, it will often contain nearly 10 per cent. more water than the same species of timber cut in the winter. For instance,—

Wood	Cut in January. Water.	Cut in April.* Water.
Ash	28.8	38.6
Sycamore	33.7	40.3
Horse chesnut	40.2	47.1
White fir	52.7	61.0

It also varies in quantity according to the species of tree, the average quantity of moisture present being shown in the following table :—

Water contained in 100 parts of fresh cut wood :—

Hornbeam	18.6
Willow	26.0
Sycamore	27.0
Ash	28.7
Birch	30.8
Oak	34.7
Horse chesnut	38.2
Pine	39.7
Elm	44.5
Larch	48.6
Poplar	51.8

A certain amount of this moisture can be got rid of by exposing the wood to air and at the same time protecting it from rain, but under favourable circumstances, and after a year's exposure, air dried wood will still contain about 20 per cent. of moisture, whilst after several years keeping in a warm room it will often retain 17 per cent. of moisture.

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* Schubler and Neuffer.

For all practical purposes, therefore, wood will, under favourable circumstances, only contain 80 per cent. of solid matter, whilst the large amount of heat absorbed in heating and evaporating the water present is a serious drawback to its employment as a fuel. The ash left on burning wood varies from ½ to 5 per cent., and an excess of ash as it is incombustible, must be looked upon as diminishing the value of wood for heating purposes.

The amount of combined oxygen present in any fuel seriously detracts from its value, as its presence means that some of the combustible constituents of the fuel have already been used up by the oxygen, and are no longer available for generating heat.

Wood when heated out of contact with air yields a variety of volatile products and leaves a residue of charcoal. This charcoal is not pure carbon; it always contains oxygen, hydrogen, and a small quantity of nitrogen in addition to the mineral constituents or ash of the wood, but the moisture and a large percentage of the combined oxygen having been got rid of, the charcoal is bulk for bulk a much more valuable fuel than wood, so that in cases where great local heat is required, it is preferable to convert the wood into charcoal before using it. Charcoal which is to be used as fuel is nearly always prepared in this country in charcoal heaps, in which the combustion of some of the wood subjects the remainder to destructive distillation, air being as far as possible excluded by coating the heap with clay or loam. During the partial burning of the heap, some moisture is distilled off as water, whilst the combined oxygen and most of the hydrogen escape, partly combined together and partly combined with carbon as tar, naphtha and other hydrocarbons which distil out of the heap and are lost. In foreign countries, however, wood is frequently subjected to destructive distillation almost entirely for the sake of the tar (Stockholm tar) and pyroligneous acid which are evolved, and in order to collect these substances, the carbonisation is carried on in closed vessels. When the charcoal is to be used for the manufacture of gunpowder, it must be prepared with great care, and at a low temperature; superheated steam being often employed as the heating power. The rate at which the carbonisation takes place has a great effect upon the yield of charcoal obtained; with rapid heating there is a considerable loss, not more than from 17 to 20 per cent. by weight of charcoal being obtained, whilst with careful heating, as much as 25 per cent. of the weight of the wood taken remains as charcoal.

As a fuel charcoal has about double the calorific value of air dried wood.

Another kind of fuel much employed for domestic purposes in certain parts of the world is peat, which is composed of vegetable matter, generally mosses and aquatic plants, which, under the combined agency of time and pressure, have been converted into the spongy brownish black substance found in the peat bogs. This peat is cut out in long square blocks, and is piled up exposed to air until dry. The relative heating power of dense, well dried peat is about the same as wood and half that of coal. In composition peat occupies a position intermediate between wood and coal, and there is no doubt that the formation of peat is a stage in the great natural process by which woody fibre is converted into the most valuable of our fuels—coal.

Coal is now ascertained to be of entirely vegetable origin, and is the remains of a vegetation which covered the land long before it was inhabited by man. This vegetation has undergone partial decomposition and has been covered by accumulations of clay and sand; the pressure of these deep overlaying strata has prevented the evolution of gas, and has destroyed most traces of vegetable structure and given to the pit-coal its close and compact form; but ample proof of its origin is to be found in the strata immediately above the coal seams, which abound in the fossil remains of upwards of five hundred different kinds of mosses and ferns, whilst in the layer immediately below the seam, fossil roots are found in abundance.

The three principal varieties of coal are lignite, bituminous coal, and anthracite, the lignite or brown coal being the least carbonised, showing indications of organised structure, and containing considerable proportions of hydrogen and oxygen; whilst anthracite is the most carbonised, and often contains little else than carbon and the mineral matter or ash.

When moist vegetable matter undergoes fermentation and decay, carbon dioxide and marsh gas are the gaseous compounds which escape, and it is easily conceivable that the final action taking place during long ages, aided by pressure and the internal heat of the earth, is the conversion of woody fibre into carbon in the dense form known to us as graphite; whilst intermediate steps in the decomposition give us peat, lignite, bituminous coal and anthracite. The complete reaction could be represented by the equation:—

$$\overset{\text{Woody fibre}}{2(C_6H_{10}O_5)} = \overset{\text{Carbon dioxide}}{5(CO_2)} + \overset{\text{Marsh gas}}{5(CH_4)} + \overset{\text{Carbon.}}{C_2},$$

which is supported by the fact that these two gases are always found in the coal seams. The theory that bituminous coal is a "younger coal" than anthracite is not, however, borne out by the fact that in the eastern part of Wales the coal is of a bituminous nature, gradually shading away into the anthracite, found in the western portion of the Principality, as it is extremely unlikely that there is any very great difference in the age of the different parts of the Welsh coal field.

The gradual conversion of woody fibre into peat, coal and graphite, is illustrated by the following table, in which to show the gradual elimination of hydrogen and oxygen, the carbon is kept as a constant number :—[*]

	Carbon	Hydrogen	Oxygen.
Wood	100	12.18	88.07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal	100	6.12	21.23
Anthracite (Wales)	100	4.75	5.28
,, (Pennsylvania)	100	2.84	1.74
Graphite	100	0.00	0.00

The amount of hydrogen present in a fuel exercises an important influence upon the way in which it burns, as hydrogen is expelled at a fairly low temperature in combination with some of the carbon as gases which are inflammable at a moderate temperature; the burning gas surrounds the fuel and continues to heat it, whilst the escape of the gas leaves the remaining and less inflammable carbon in a porous condition, which is favourable to carrying on the combustion. Flame is burning gas, and therefore the nearer to pure carbon that our fuel approaches, the less the amount of flame produced by its combustion, because the smaller will be the quantity of inflammable gas evolved.

Lignite contains more hydrogen than any other variety of coal, and is for this reason more easily ignited and burns with more flame than any of the others; the next in this respect being the bituminous coals such as the Silkstone and Wallsend, whilst the anthracites are difficult to ignite, and when lit, can only be kept burning by a strong draught, this rendering them unfit for use in ordinary grates.

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[*] Percy.

The tarry products which distil out of bituminous coals when heated, cause them to cake together, and this property enables the dust to be used for firing if certain precautions be taken.

It has been decided by a Commission appointed to consider the characteristics of a good coal for Service purposes, that it should possess: *

1. High evaporative power.
2. The property of burning readily with a moderate draught.
3. It must not produce much smoke, which in time of war would reveal the whereabouts of the ships; and it must not cake enough to choke the fire bars.
4. It must be cohesive; or if it break up on heating, should cake moderately.
5. It should be dense, so that in storing it does not take up too much room.
6. It should be free from any large proportion of sulphur or sulphur compounds, and on burning should leave but little ash.

And in order to ascertain the relative merits of the various coals in the market, an exhaustive series of trials were made under the conditions then in vogue.

For the evaporating power and rate of evaporation a Cornish boiler was used, and the average of a large number of trials taken with the following results:—

	A	B	C	D	E	F
Welsh Coal ...	9·05	448.2	53·1	42.71	60.9	1.42
Newcastle ,, ...	8.37	411.1	49.8	45·3	67.5	0.94
Lancashire ,, ...	7·94	447·6	49·7	45·15	73·5	1.42
Scotch ,, ...	7·70	431.4	50.0	49·99	73·4	1.45
Derbyshire ,, ...	7·58	432·7	47·2	47·45	80.9	1.01

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* British Commission on Fuel, 1851.

A. Evaporating power.
B. Number of pounds evaporated per hour.
C. Weight of a cubic foot of the coal as used.
D. Number of cubic feet occupied by one ton.
E. Cohesive power (*i.e.*, percentage of large coal).
F. Percentage of sulphur.

From these results it is evident that the Welsh and North Country coal most nearly approach the standard required, and in order to combine as far as possible the merits of each class of coal, a mixture of $\frac{2}{3}$rds Welsh and $\frac{1}{3}$rd North Country coal was generally adopted for use in the Navy.

The introduction of new forms of engines and boilers and the use of a forced draught, have however, at the present time, rendered the necessity for the coal burning well with a moderate draught less important, whilst the cohesive power of coal is not now a factor of the same importance; and at the same time the evaporative power and freedom from smoke, ash, and caking become of increased importance, with the result that little else than Welsh coal is now used in the Service.

The stowage values as recognised in the Navy are not quite the same as those given in the table, a ton of Welsh coal being estimated to fill 40 cubic feet of space, and the Newcastle coal 43 cubic feet. It is most important that in a coal for Service use there should be as little sulphur present as possible, as the general form in which it occurs is iron pyrites—a sulphide of iron which may be represented by the formula FeS_2—and in the presence of moisture and air, this compound undergoes oxidation and generates considerable heat, which, if the action takes place in the centre of a large mass of coal, sometimes causes spontaneous combustion, from the fact that coal is a bad conductor of heat, and the heat therefore accumulates and causes a rise of temperature at times sufficiently great to ignite the more inflammable hydrocarbons; whilst even if this point be not reached, the rise in temperature causes the escape of occluded marsh gas into the coal bunkers and increases the risk of explosion.

A more insuperable objection to the presence of sulphur in coal is, that when it is heated in the presence of iron it renders the metal fusible at a much lower temperature, and also by entering into combination with it renders the iron brittle when cold, both these actions being highly detrimental to the fire bars.

When coals containing iron pyrites burn at the high temperature of the furnace, the sulphur escapes either in combination with oxygen as sulphur dioxide, or else distils out and combines with the furnace bars or boiler plates, leaving the iron with which it was originally combined as ferric oxide.

$$\overset{\text{Iron pyrites}}{4(\mathrm{FeS_2})} + \overset{\text{Oxygen from air}}{11(\mathrm{O_2})} = \overset{\text{Ferric oxide}}{2(\mathrm{Fe_2O_3})} + \overset{\text{Sulphur dioxide.}}{8(\mathrm{SO_2})}.$$

And this residual ferric oxide colours the ash left by the coals reddish brown, a colour which is generally supposed to indicate sulphur, when it is seen in the ash.

The ash of coal consists of silica, alumina, oxide of iron, and sulphates and phosphates of lime and magnesia, varying with the description of coal from 0.5 to 30 per cent. Much ash is objectionable, as not only does it detract from the quantity of the fuel present, but also as the coal burns, the ash forms on its surface, and retards the combustion of the coal by keeping air from it.

In the same way that charcoal is obtained from wood by destructive distillation, so coke may be obtained from coal, the hydrogen and traces of other substances which it contains being driven off, on heating it out of contact with air.

When this is done in the manufacture of coal gas, the resulting coke is called gas coke, but for many metallurgical processes coke is specially prepared in ovens, temperatures being reached at which the escaping gases are of no use for illuminating purposes, and can only be used to heat boilers, etc., but at which temperatures a superior quality of coke is produced. This kind of coke is called oven coke.

The advantages of coking coal is that it yields a more intense local heat than coal, it does not cake, and the heat at which it is produced drives off a large proportion of the sulphur contained in the original coal, a most important factor in many metallurgical operations, in which sulphur, in even small traces, is most objectionable; whilst another advantage in the use of coke is that it gives off little or no smoke during combustion; it, however, requires a high temperature to ignite it, and a brisk draught in the chimney to carry on combustion, properties which render it more fitted for use in manufacturing processes than for domestic consumption.

The relation which coke bears to the coal from which it has been formed, is shown by the table on p. 177, in which the composition of coal and coke are contrasted.

The heating effects produced by coke are, by calculation, a little better than those obtained from coal; but in practice the amount of heat obtainable from coal and coke are practically the same.

Of late years the subject of liquid fuels has attracted great attention, and with the discovery of the Russian oil fields, methods of utilising this most important source of energy are daily becoming practicable; and at the present time it is already in use for generating steam, both in locomotives and ships' boilers.

The liquid fuels may be classed under two heads:

1. Petroleums:
    - Russian.
    - American.
2. Tar:
    - Heavy tar oil.
    - Dead oil.

The Russian petroleum differs from the American oil, in that it contains chiefly hydrocarbons of the series C_nH_{2n}, and also bodies called benzenes, whilst American petroleum consists of hydrocarbons of the series C_nH_{2n+2}.

The origin of the petroleum found in such enormous quantities in the oil districts of Russia and America is at present somewhat doubtful. Some consider it a product of the destructive distillation of coal at high subterranean temperatures; others, that it is derived from deposits of marine animals; whilst Professor Mendeleeff* considers that it is formed by the action of water at a high temperature and under great pressure, upon compounds of iron, manganese and carbon.

The crude petroleum on distillation yields light oils, having a flashing point of from 22° to 30° C., which are called "kerosene," and which it would of course be impossible to use for fuel on board ship on account of the inflammable vapour given off at comparatively low temperatures. After, however, the "kerosene" has been distilled off, the residue left in the retort and which is called "astatki," can by further heating be made to yield lubricating oils and also "solar oils" used for lamps. The "astatki" has a flashing point of over 100° C., and is the portion of the oil used as fuel, for which purpose it is admirably adapted, and it is now largely used in locomotives on the Russian railways, and in steamers on the Volga and Caspian Sea, giving in work an evaporating power of 12 to 13½ lb.

Theoretically the petroleums contain nothing but hydrogen and carbon, but small traces of compounds containing oxygen are generally to be found in them, the average composition of fifteen samples of petroleum from various sources being:—†

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* Revue Scientifique, 1877.

† M. Sainte-Claire Deville.

Carbon	84.7
Hydrogen	13.1
Oxygen	2.2
	100.0

As might be expected from this composition the heating value of the petroleums is very great; in a stationary boiler fitted with Nobel's troughs for burning the oil, an evaporative service of 14.5 lb. of water was obtained, whilst the same petroleum (astatki), when sprayed into the furnace by a steam injector, gave an evaporation of 12 lb. of water per lb. of oil used: coal used in the same boiler only evaporating 7 to 8 lb. of water.*

The Russian gunboats have for several years used this form of liquid fuel, and it is being adopted in some of the vessels of the Black Sea fleet. The advantages of liquid fuel for heating marine boilers are very great, and amongst them it is claimed that very little alteration in the present form of furnace is necessary, that a great reduction in weight and bulk of fuel is gained, amounting to between 30 and 40 per cent., a reduction of ¾ths the number of stokers now employed, prompt kindling and extinction of the fires, control over the temperature and absence of necessity for forced draught, freedom from smoke, and absence of ashes and dirt. The saving of time and absence of dirt, not to mention wear and tear of the interior of the coal bunkers, would be great as the liquid would be run into the ship's tanks from high level cisterns, and might be made to take the place of water ballast, the tanks as they were emptied being filled with water. The present difficulty is cost; but considering the enormous supplies now being obtained, a rapid reduction in price may be looked for. Petroleum at 1d. per gallon would be equal in cost to coal at 16/3 per ton as a fuel, but considering the enormous saving of time and labour, it is evident that petroleum at a much higher price would be a very advantageous substitute for coal.

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* Boverton Redwood, Society of Chemical Industry, 1885.

Heavy tar oil, the distillate coming over from tar after the separation of the lighter oils, known commercially as "creasote," has many properties which recommend it as a liquid fuel, as is also the case with the residual products of the distillation of shale oil, which up to the present time has been practically a waste product. These heavy oils have of late been used for spray burners for illumination, such as the Lucigen and Doughty lights, in which the heavy oil is sucked up, sprayed, and burnt by a blast of compressed air from a reservoir, and the same principle can be effectively used for heating purposes, as is shown by the use of such burners for rivet heating, etc., in all the work on the Forth bridge.

Tar itself makes a very effective liquid fuel, but its viscosity renders it necessary to employ injectors and valves of special construction.

From experiments lately carried out by Mr. Holden, of the Great Eastern Railway, it appears that the most effective way of using liquid fuel is to inject it into the fire box, either of locomotive or marine boilers, above a thin layer of incandescent fuel, and when used in this way, complete combustion and almost entire absence of smoke is attained.

For this purpose the heavy tar oil, or the "astatki" would be sprayed into the fire box by means of a steam injector (Fig. 38) in which steam being forced through the tube (A), would draw the oil up the supply tube (B), and spray it over the burning fuel.

This method of using liquid fuel as an adjunct to solid fuel is well adapted for marine boilers as, if through any cause a breakdown in the arrangements for the supply of liquid fuel took place, it could at once be replaced by coal, by merely removing the injector.

The utilisation of gases as fuel has from time to time ttracted a large amount of attention, and in many processes nd under certain conditions, the use of gaseous fuel presents many advantages.

The gaseous fuels tried, and to a certain extent adopted, in England, are of three kinds :—

1. Ordinary coal gas.
2. Water gas.
3. Generator gas.

nd of these, coal gas has during the last few years been used ery largely as a fuel for domestic purposes, such as heating nd cooking, with very good results, the only drawback being he cost of gas as compared with coal as a fuel. When used or such purposes the gas is burnt mixed with air in tmospheric burners, and during complete combustion a very igh temperature is attained ; but per unit of heat evolved the ost is about three times that of coal, against which, however, must be set the economy of being able to turn on the gas just hen required, and to turn it off when the desired effect as been produced, and this when taken in conjunction ith the saving of labour, and absence of dirt and smoke, onsiderably decreases the margin in favour of coal.

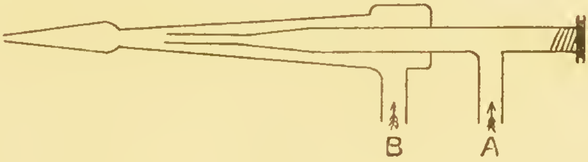

Fig. 38.

It has often been said that a heating gas could be pro-uced at a cost of about ⅓rd that of illuminating gas, that is, hat a much larger volume of gas power in hydrocarbons ould be obtained from a given weight of coal, but it must not e forgotten that the chief expenses in the manufacture of lluminating gas, are the wear and tear of plant, labour, distribution of gas, and other items of like character which would be as great, if not greater when making heating gas; and that although there might be a considerable saving in coals, yet that the fixed charge on the plant used would remain, and would practically prevent the enormous reduction in cost hoped for.

In all cases where gas is used to heat metallic surfaces, care should be taken to provide ample ventilation, and all gas stoves should be connected with a flue to remove products of combustion, as when the combustion of an atmospheric burner is checked by the flame coming in contact with a cold metallic surface, carbon monoxide is invariably formed and being of an extremely poisonous nature, even minute traces in the air of a room, are injurious to health.

Water gas depends for its formation upon the fact that at high temperatures carbon has a greater affinity for oxygen than hydrogen has, and that when steam and carbon (in any of its amorphous forms) are heated to such a temperature, the steam is decomposed with liberation of hydrogen and either carbon monoxide or dioxide, the oxide formed being to a great extent dependent on temperature, and the quantities of steam and carbon interacting.

The action may be represented as follows :—

$$\overset{\text{Carbon}}{C} + \overset{\text{Steam}}{H_2O} = \overset{\text{Carbon monoxide}}{CO} + \overset{\text{Hydrogen.}}{H_2}$$

or—

$$\overset{\text{Carbon}}{C} + \overset{\text{Steam}}{2(H_2O)} = \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Hydrogen.}}{2(H_2)},$$

and the value of the gas produced, as a fuel, largely depends upon the closeness of approximation to the first reaction, but the ideal composition is rarely if ever reached, water gas practically consisting of a mixture of carbon monoxide and dioxide, hydrogen and small quantities of marsh gas, formed by the direct combination of the liberated hydrogen and carbon.

Attempts which were made to introduce water gas on a large scale in Paris, failed from fear of the poisonous properties of its chief constituent, carbon monoxide; whilst the adoption of water gas in America has not proved it to be a financial success. There are two methods employed on a large scale for its preparation; the first being to heat the carbon and steam together in retorts to a high temperature, by means of external firing, whilst in the second, carbon is raised to incandescence in a chamber by means of an air blast which forms a mixture of carbon monoxide and nitrogen, and then steam is blown through it until its temperature falls to a dull red heat, when it is again revived by the air blast, and again acted on by steam, the process being an alternate partial combustion in air, and treatment with steam.

Generator gas is a mixture of carbon monoxide and nitrogen, having the theoretical composition:—

Carbon monoxide	34·3
Nitrogen	65·7
	100.0

and is the least efficient of the gaseous fuels. It is formed by passing air through a column of heated coke, when the carbon at the lower surface of the column burns to carbon dioxide, combining with the oxygen of the air; and the carbon dioxide, by contact with the heated carbon over which it has to pass, is then reduced to carbon monoxide:—

$$\begin{array}{ccccccc} \text{Carbon} & & \text{Air} & & \text{Carbon dioxide} & & \text{Nitrogen} \\ C & + & 2(N_4+O) & = & CO_2 & + & 4(N_2) \end{array}$$

and

$$\begin{array}{ccccc} \text{Carbon dioxide} & & \text{Carbon.} & & \text{Carbon monoxide.} \\ CO_2 & + & C & = & 2(CO), \end{array}$$

the carbon monoxide and residual nitrogen from the air forming the "generator gas."

The heating power of such a gas is very low, but its production is inexpensive, and it is therefore found convenient to use it as a source of heat in certain manufacturing operations in which great intensity is not an object.

The heat generated during the combustion in oxygen of substances which will combine with that element, was first accurately determined by Andrews* and also by Favre and Silberman† some forty years ago, and they represented the results obtained by the number of unit weights of water which a unit weight of the fuel, during combustion, could raise from 0° C. to 1° C., and the amount of heat necessary to raise a unit weight of water from 0° C. to 1° C. is called a thermal unit.

HEAT DEVELOPED DURING COMBUSTION IN OXYGEN.

Combustible	Products of combustion.	Thermal units evolved.
Hydrogen	Water	34,400
Carbon	Carbon dioxide	8,080
Carbon monoxide	,, ,, ...	2,400
Marsh gas	Carbon dioxide and water ...	13,063
Olefiant gas	,, ,, ,, ...	11,850

When a fuel consists of carbon and hydrogen only, it is considered sufficiently accurate in practical working to determine its composition, and then to multiply the carbon present by 8,080, and the hydrogen by 34,400, the sum of the numbers so obtained being taken as representing the calorific value of it as a fuel; for instance, on analysing marsh gas, we find that it has a percentage composition of—

Carbon	75
Hydrogen	25
	100

and

$$\frac{(75 \times 8080) + (25 \times 34400)}{100} = 14660.$$

14660 would therefore be taken as the calculated calorific value of marsh gas.

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* *Phil. Mag.*, 1848.

† *Ann. Chem. Phys.*, 1852.

This method of calculation is open to many objections, which will be discussed later on, and is much more complicated when we have to take into consideration the presence of combined oxygen, and the loss of heat entailed by the presence of moisture.

Taking the case of dry cellulose, we have present 44.44 per cent. of carbon, and 6.17 of hydrogen; but there is also present 49.39 of oxygen, and as this oxygen has already entered into combination with the carbon and hydrogen present, the quantities of these elements so combined are no longer available for the generation of heat during combustion.

Oxygen combines with $\frac{1}{8}$th of its weight of hydrogen to form water, and if we look upon all the oxygen present as being combined with hydrogen, the calorific value would be found from the following formula:—

$$(C \times 8080) + \left\{\left(H - \frac{O}{8}\right) \times 34400\right\}$$

which, applied to cellulose, would give us—

$$\frac{(44.44 \times 8080) + \left\{\left(6.17 - \frac{49.39}{8}\right) \times 34400\right\}}{100}$$

$$= \frac{4444 \times 8080}{100} = 3590.7.$$

In other words, the oxygen present in combination is sufficient to entirely use up the hydrogen, and the calorific value of the fuel is practically the value of the carbon present. It is evident therefore that combined oxygen in a fuel means that a certain percentage of it is not available as a fuel, having been already burnt up, and the disadvantage of it is still more clearly seen when we come to calculate the practical value of a fuel. The numbers so far obtained are thermal units: that is, when we say the calculated calorific value of cellulose is 3590.7, we mean that one pound of cellulose, in burning to carbon dioxide and water, evolves sufficient heat to raise 3590.7 lb. of water from 0° C. to 1° C., and this gives an idea of the relative values of the various fuels, but very little idea of what the fuel might be expected to do in practice. For instance, to a working engineer the amount of water which can be raised from 0° C. to 1° C. is a matter of perfect indifference; but it is often of value to find how much water can be raised from the ordinary temperature and converted into steam, allowance having to be made for the heat necessary to convert the water into steam, at the pressure existing in the boiler, and also for the heating and evaporation of water present as moisture, and formed by the combined oxygen present, and a formula used in this way to determine the evaporative power of a fuel is

$$\frac{C \times 8080 + \left\{ \left(H - \frac{O}{8}\right) 28780 \right\} - (H_2O \times 600)}{536.5 \times 100}$$

the H_2O being the moisture present.*

Applying this in practice to a sample of Silkstone coal, we first determine its percentage composition, and find it to be—

SILKSTONE COAL.†

Carbon	79.0
Hydrogen	5.2
Nitrogen	1.5
Sulphur	1.5
Moisture	4.0
Ash	2.8
Oxygen	6.0
	100.0

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* In the Service and Mercantile Marine the Fahrenheit scale is still retained and the evaporative value is mostly calculated from the percentage composition by the formula,

$$0.15 \left\{ C + 4.28\left(H - \frac{O}{8}\right) \right\}$$

† Lewis T. Wright. *Journal Soc. Chem. Industry*, 1887.

Then using the formula, we have—

$$\frac{79 \times 8{,}080 + \left\{\left(5.2 - \frac{6.0}{8}\right) \times 28{,}780\right\} - (4.0 \times 600)}{536.5 \times 100} = 14.24,$$

or a theoretical evaporative power of 14.24 lb. of water per lb. of fuel consumed.

All such calculations are, however, of little value, as they give results far higher than can be obtained by practical experiment, however carefully conducted. In a recent paper by Mr. Lewis Wright, the following table contrasting the actual and calculated evaporating power of two kinds of coal, and the coke from them is given :—

	Actual	Calculated	Per cent.
Nottingham top hard Cannel coal	8.78	12.27	71.56
Yorkshire Silkstone coal	10.01	14.24	70.30
Top hard Cannel coke	9.91	12.23	81.03
Silkstone gas coke	11.15	13.83	80.62

Showing that the calorific value as calculated for the two samples of coke approaches much more nearly to the actual value than in the case of the coal from which the coke had been made.

Mr. Wright also gives the percentage composition of the coals and cokes, and on tabulating these, we see that the more closely the fuel approaches the condition of pure carbon, and the greater the quantity of hydrogen eliminated, the more closely the actual and calculated results agree.

	Nottingham T.H. Cannel.	Yorkshire Silkstone.	Cannel coke.	Silkstone coke.
Carbon ...	67.0	79.0	80.1	89.0
Hydrogen ...	5.6	5.2	0.6	1.0
Nitrogen ...	1.2	1.5	1.3	1.0
Sulphur ...	1.0	1.5	0.4	1.2
Moisture ...	7.6	4.0	4.1	1.2
Ash... ...	6.6	2.8	11.9	5.2
Oxygen ...	11.0	6.0	1.6	1.4
	100.0	100.0	100.0	100.0

The causes of these discrepancies are two-fold—in the first case during actual experiment, it is almost impossible to avoid the loss of a certain amount of heat, whilst the second cause at once condemns all methods of calculating heating powers at present in use. Woody fibre, wood, peat and coal, are all more or less definite chemical compounds, and in order to break them up during combustion, as much heat is absorbed as was originally given out during their formation; this heat should be allowed for, and the allowance can be made in a few simple cases, as in the case of marsh gas.

Calculating, as before shown, the heating effect of marsh gas, we find that it has a thermal value of 14,660 units, but the heat of formation of the molecule of marsh gas (CH_4) is $+$ 20,414 thermal units, and our value for marsh gas so corrected would be $14{,}660 - \frac{20{,}414}{16}$, or 13,384 thermal units, a number much more nearly approaching that obtained by actual experiment.

We do not however know the heat of formation of coal and many other fuels, and therefore all calculations of their calorific effects must be erroneous and misleading, and can only be accepted as showing in a rough way their relative values as fuel.

Many methods have been proposed for the experimental determination of the heating effects of fuel, and amongst purely chemical methods, the process devised by Berthier was the most used; it consists of heating a known weight of the fuel to be tested with 70 times its weight of oxide of lead (litharge) and some oxychloride of lead, when the carbon and hydrogen of the fuel burn at the expense of the oxygen of the lead oxide, reducing it to metallic lead, which can then be recovered and weighed. This process, however, gives very unsatisfactory results, the hydrogen only showing the same calorific value as carbon; whilst impurities in the litharge and crucible used further interfere with the accuracy of the results obtained.

An easier and more satisfactory method is the determination of the heat evolved by Thompson's calorimeter; in which the fuel to be tested is burnt by combined oxygen in a small metal diving bell, under the surface of a known weight of water, and the calorific value is then determined by the increase in temperature of the water.

These instruments are graduated for use with the Fahrenheit thermometer, and on this scale the latent heat of steam is 967, that is to say, the amount of heat rendered latent in converting a pound of water at 212° F. into steam at the same temperature, would raise 967 lb. of water 1° F. It is clear then that if a unit weight of fuel is burnt under the surface of 967 unit weights of water, and if all the heat is imparted to the water and raises it one degree, the same amount of heat would have converted a unit weight of water at 212° F. into steam at the same temperature. In practice 2 grams of the fuel in a finely divided condition are taken, and having been mixed with 11 times the weight (22 grams) of a finely powdered mixture of chlorate of potash and nitrate of potash (3 of the former to 1 of the latter)—which is to supply the oxygen for its combustion—it is then, after careful mixing, pressed a little at a time into a small brass crucible. When the mixture is all introduced, a small fuse, made of cotton soaked in nitrate of potash, is placed in a cavity in the top of the mixture, and the crucible is then fixed by means of a brass plate and clutch springs in the mouth of the diving bell or condenser; having first ignited the fuse, the whole arrangement is then plunged under the surface of $967 \times 2 = 1934$ c.c. of water of known temperature. The fuse ignites the mixture and the fuel burns at the expense of the combined oxygen present in the chlorate and nitrate of potash, and the products of combustion escaping through small holes in the bottom of the condenser pass up through the water, and are supposed in this way to be cooled. When the combustion is complete the water is admitted to the condenser by opening a tap in a tube connected with it, when the water rushes in and cools the crucible; after having well agitated the water by raising and lowering the whole apparatus several times so as to obtain a uniform temperature, the apparatus is withdrawn and the thermometer again inserted and the rise of temperature observed. Ten per cent. is now added to the number so obtained to make up for loss of heat absorbed by the apparatus, radiation, etc., and the total is looked upon as giving the number of unit weights of water which a unit weight of the fuel would evaporate. For instance—

Temperature of water before combustion =	62° F.
,, ,, after ,,	75° F.
Rise in temperature	13
10 per cent.	1.3
Evaporative power =	14.3

And as a gram of the fuel will evaporate 14.3 grams or c.c. of water, therefore one pound will evaporate 14.3 lb. Two of the objections to the method are, that the rapidity with which the gases escape during the combustion renders it impossible that they should be entirely cooled by the water through which they bubble, as only the outside of them is in actual contact with the water, and also that when the water is heated to a temperature much above that of the room there will be a further loss by radiation, an objection which can be to a considerable extent met by performing the operation with the initial temperature of the water 8° to 10° F. lower than the temperature of the room.[*]

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[*] J. W. Thomas. *Chem. News*, 1881.

The calorific value of a fuel is very different from its calorific intensity, which is entirely dependent upon the rate of burning. It must be remembered that a pound of wood, when completely converted into carbon dioxide and water vapour, will, during the process of conversion, give out a certain quantity of heat; and that the same amount of heat will be given out, whether the wood slowly rots away by slow combustion, is burnt in an open grate, or in a furnace, urged on by a blast of air. In each case the total amount of heat given out is the same, but the intensity in each case is very different. The shorter the space of time in which the complete combustion of the wood takes place, the greater will be the intensity of the heat.

It must also be remembered that besides having to vaporise moisture, the combustion of the fuel has also to raise the carbon dioxide (formed by the burning carbon) and the residual nitrogen of the air used, to a high temperature; and this must be allowed for in any calculation which is to at all fairly express the heat available for other purposes.

CHAPTER XI.

NITROGEN AND ITS COMPOUNDS.

Nitrogen, occurrence in Nature—Preparation—Properties of nitrogen—Ammonia—Formation in Nature—Preparation and properties of the gas—Liquid ammonia—Decomposition of ammonia—Ammonia salts—Ammonium amalgam—The oxides of nitrogen—Preparation and properties of nitrogen monoxide, dioxide, trioxide, tetroxide, pentoxide—Nitric acid—Oxidising action of nitric acid—Classification of salts—Tests for nitrogen.

NITROGEN was first discovered by Rutherford in 1772, and its properties were afterwards fully examined by Scheele and Lavoisier, the latter giving it the name "azote," from its inability to support life; the name "nitrogen" being given to it at a much later date, to denote that it was one of the principal ingredients of potassic nitrate or nitre.

Nitrogen constitutes 79.1 per cent. by volume, and 76.9 per cent. by weight of the atmosphere; and is also found widely distributed as nitric acid and metallic nitrates, as well as in ammonia and in animal and vegetable organisms.

It can be prepared from air by taking away the oxygen, and this can be conveniently effected by burning some phosphorus in a jar of air standing over water. The phosphorus combines with the oxygen of the air, forming white fumes of phosphoric pentoxide, which dissolve in the water, leaving fairly pure nitrogen gas behind.

$$\underset{\text{Phosphorus}}{P_2} + \underset{\text{Air}}{5(N_4+O)} = \underset{\text{Phosphoric pentoxide.}}{P_2O_5} + \underset{\text{Nitrogen}}{10N_2}.$$

Air may also be passed over copper turnings heated to redness, when the copper takes up the oxygen, forming cupric oxide, and nitrogen passes on free.

If it is required perfectly pure it is made from a compound called ammonic nitrite, which, when heated, breaks up into water and nitrogen.

Ammonic Nitrite Water Nitrogen.

$$NH_4NO_2 = 2(H_2O) + N_2.$$

If a stream of chlorine gas, generated by the action of hydrochloric acid on black oxide of manganese, be led through a saturated solution of ammonia, nitrogen is liberated, and the hydrochloric acid produced unites with some of the ammonia to form ammonic chloride.

Ammonia Chlorine Ammonic Chloride Nitrogen.

$$8(NH_3) + 3Cl_2 = 6(NH_4Cl) + N_2.$$

When nitrogen is prepared in this way, it is important to keep the ammonia in excess, as, if chlorine were to predominate, it would react upon the ammonic chloride, and form a highly explosive combination of chlorine and nitrogen, called nitrogen trichloride.

A very usual way to prepare the gas is by heating together saturated solutions of potassic nitrite and ammonic chloride, when—

Potassic nitrite Ammonic chloride Potassic chloride Water Nitrogen.

$$KNO_2 + NH_4Cl = KCl + 2(H_2O) + N_2.$$

The gas can be collected over water as it is very sparingly soluble, 100 volumes of water only dissolving 1.5 volumes of the gas at ordinary temperatures.

Nitrogen in the free state is the most inert of gases, and is characterised by its inability to burn or to support combustion, and generally by its disinclination to combine directly with common substances.

If we measure off 11.16 liters of the gas at normal temperature and pressure we find that it weighs 14 grams, and is therefore, atom for atom, 14 times as heavy as hydrogen.

It is a colourless, tasteless and odourless gas, which will not support life.

It is evident that it has no poisonous properties as our atmosphere contains so large a proportion of the gas.

Although so inert in its relations towards most substances, it combines with the elements tungsten and titanium with great energy, converting them into nitrides and causing them to become incandescent when they are thrown in a finely divided state into a jar of the gas, and it also forms compounds with boron, silicon and magnesium.

Nitrogen cannot be readily made to unite directly with hydrogen, but by indirect means an important compound of nitrogen and hydrogen can be obtained, viz.: ammonia gas.

In Nature ammonia is chiefly produced during the spontaneous decomposition of nitrogenised organic matter, such as animal excreta, and the name ammonia was given it because the Arabs first prepared it from camel's dung, near the temple of Jupiter Ammon in the Libyan desert. Ammonia is found during the manufacture of coal gas as one of the bye-products, and is obtained in combination with hydric chloride as sal ammoniac or chloride of ammonium, and it is from this salt that we can most conveniently obtain the gas. If we mix together powdered chloride of ammonium and quicklime and gently heat the mixture, ammonia gas is given off and calcic chloride and water are formed.

$$\overset{\text{Ammonic chloride}}{2(NH_4Cl)} + \overset{\text{Quicklime}}{CaO} = \overset{\text{Calcic chloride}}{CaCl_2} + \overset{\text{Water}}{H_2O} + \overset{\text{Ammonia.}}{2(NH_3)}.$$

Ammonia gas so prepared cannot be collected over water, on account of its great solubility, water dissolving 1,149 times its own volume of the gas at normal temperature and pressure.

It is best collected over mercury, but being much lighter than air can also be collected by upward displacement in the same way as hydrogen.

Ammonia gas is readily recognised by its pungent odour and strong alkaline reaction, turning yellow turmeric paper brown, and red litmus paper blue. The test papers which have been acted upon however, soon regain their original colour when exposed to air, as the ammonia rapidly volatilises, hence it is sometimes called a "volatile alkali." The gas does not support combustion, nor does it burn in the ordinary sense of the word; but if it be ignited in oxygen, it readily burns with a non-luminous flame forming water and liberating nitrogen; and a mixture of ammonia and oxygen will explode when a light is applied to it, the products of the explosion also being nitrogen and water:—

$$\begin{array}{ccccccc} \text{Ammonia} & & \text{Oxygen} & & \text{Nitrogen} & & \text{Water.} \\ 4(NH_3) & + & 3O_2 & = & 2N_2 & + & 6(H_2O). \end{array}$$

When ammonia gas comes in contact with hydrochloric acid gas, dense white fumes of ammonic chloride are formed.

Ammonia gas can be liquefied by a pressure of about seven atmospheres, and this liquid if cooled below—75° freezes to a transparent solid.

The ease with which ammonia can be liquefied, the great cold produced when it again assumes the gaseous state, and the amount of the gas dissolved by water, renders it eminently adapted for use in freezing machines, one of the best known of which is "Carré's ice making apparatus," in which ammonia, evolved by boiling a strong solution of the gas, is condensed by pressure in a strong iron reservoir, in the centre of which is a chamber to receive the substances to be frozen. The pressure is then taken off the iron reservoir and the liquid ammonia once more rapidly assumes the gaseous state, producing so intense a cold that water, etc., placed in the chamber is frozen. The escaping gas is once more absorbed in cooled water and can be utilised again and again.

If ammonia gas be passed through a red hot tube, or if electric sparks be passed through it for some time, its volume is doubled, and on analysis is found to consist of a mixture of one volume of nitrogen and three of hydrogen, hence the formula NH_3 is given to the gas. 22.32 liters of the gas at normal temperature and pressure are found to weigh 17 grams, hence its density as compared with hydrogen is $\frac{17}{2}$ or 8.5.

Ammonia acts as a strong base, being able to neutralise the strongest acids, forming with them salts analogous in composition to the salts formed by potassium or sodium.

Ammonia		Hydrochloric acid		Ammonic chloride.
NH_3	+	HCl	=	NH_4Cl.
Ammonia		Nitric acid		Ammonic nitrate.
NH_3	+	HNO_3	=	NH_4NO_3.
Ammonia		Sulphuric acid		Ammonic sulphate.
$2(NH_3)$	+	H_2SO_4	=	$(NH_4)_2SO_4$.

If these ammonium salts are contrasted with the corresponding potassium or sodium salts, it will be seen that in them the metal potassium (K) or sodium (Na) is replaced by the group (NH_4).

Chlorides	Sulphates	Nitrates.
$NaCl$	Na_2SO_4	$NaNO_3$
KCl	K_2SO_4	KNO_3
NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3

So strong is the analogy between them that this group (NH_4) is often looked upon as a metal, and is called ammonium, its salts being called ammonic salts.

If a strong solution of ammonia is electrolysed, the negative pole being in contact with some mercury in the bottom of the cell, and the positive above it in the liquid, the mercury swells up into a bulky buttery mass, which still retains its metallic appearance, and on allowing this to stand it evolves ammonia gas and hydrogen and once more contracts to its original volume. This experiment was considered by Berzelius to show that ammonium (NH_4) was liberated at the negative pole and formed an amalgam with the mercury, but all attempts to isolate the ammonium have so far failed.

Another way of forming this "ammonium amalgam" is to put some freshly prepared sodium amalgam into a saturated solution of ammonic chloride, when sodium is replaced by ammonium and the amalgam at once swells up to many times its former bulk, forming a spongy substance lighter than water, whilst sodic chloride passes into solution.

Ammonium compounds may be recognised by their giving off ammonia gas when heated with a strong alkali such as sodic hydrate, the gas evolved being identified by its pungent odour, and by its forming white fumes with hydrochloric acid gas.

Strong solutions of these salts also give a yellow crystalline precipitate with a solution of platinic chloride, and a white crystalline precipitate with a saturated solution of sodic hydric tartrate.

When through a mixture of oxygen and nitrogen a series of electric sparks is passed for some time, a gradual combination of the two gases takes place, and reddish brown fumes form in the vessel. The tendency however to combine is very slight; but by indirect methods, oxygen and nitrogen can be obtained in combination in five distinct proportions, as :—

Nitrogen monoxide	N_2O
Nitrogen dioxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide	NO_2 or N_2O_4
Nitrogen pentoxide	N_2O_5

Nitrogen monoxide, nitrous oxide, or laughing gas, is prepared by heating ammonic nitrate, the salt formed when nitric acid is neutralised with ammonia, and this breaks up into nitrogen monoxide and water.

$$\underset{\text{Ammonic nitrate}}{NH_4NO_3} = \underset{\text{Nitrogen monoxide}}{N_2O} + \underset{\text{Water.}}{H_2O.}$$

The gas is best collected over hot water or water saturated with salt, as cold water dissolves more than two-thirds its own volume of the gas. It is colourless and odourless, but has a sweetish taste; when inhaled it produces a kind of intoxication, hence its name; it is also used as an anæsthetic in slight operations. It can be condensed to a liquid at a pressure of 30 atmospheres, or if cooled down to—88° C.

The gas will not burn; but if a combustible be burning with vigour, nitrogen monoxide will support its combustion nearly as freely as oxygen, the heat of the burning body tending to decompose the gas and liberate oxygen, which then supports the combustion. If feebly burning sulphur be plunged into the gas, it is extinguished because the heat is not sufficient to effect decomposition; but if the sulphur be burning strongly, then it continues to burn in the gas with increased brilliancy.

When carbon is burnt in nitrogen monoxide, more heat is evolved than when it is burnt in oxygen, showing that the decomposition of the monoxide is attended with liberation of heat, and it is therefore called an "endothermic" compound.

Nitrogen monoxide can easily be distinguished from oxygen by shaking it up with water, which absorbs the former, but would not appreciably diminish the bulk of oxygen, and also by bringing it in contact with nitrogen dioxide which forms red fumes with oxygen but none with the monoxide.

Potassium or sodium heated in the gas burns with formation of potassic or sodic oxide, and the residual nitrogen is found to occupy the same volume as the nitrogen monoxide used; and as its molecular weight is 44, it is evident that the molecule contains 2 atoms of nitrogen to one of oxygen, and its formula therefore is N_2O.

Nitrogen dioxide or nitric oxide is a colourless gas obtained by acting upon metallic copper with hydric nitrate. The reaction which takes place may be represented by the equation:

$$\overset{\text{Copper}}{3Cu} + \overset{\text{Hydric nitrate}}{8(HNO_3)} = \overset{\text{Cupric nitrate}}{3\left[Cu(NO_3)_2\right]} + \overset{\text{Water}}{4(H_2O)} + \overset{\text{Nitric oxide.}}{2(NO).}$$

In contact with oxygen, nitric oxide instantly forms red fumes; it is insoluble in water, does not burn, and only supports the combustion of bodies which are burning very fiercely.

It will extinguish a burning splint of wood or burning sulphur, but phosphorus when burning fiercely is able to decompose it, and burns with increased brilliancy.

It is the most stable of the oxides of nitrogen, a low red heat not sufficing to break it up; it may be slowly decomposed into its constituents by a series of electric sparks. Nitrogen dioxide is readily absorbed by solutions of ferrous salts, forming a dark brown compound, which is decomposed by heat. When potassium or sodium is burnt in the gas, the oxygen is absorbed and the residual nitrogen is found to occupy one half the volume of the original gas. The molecular weight of the gas is 30, and it is therefore built up of one atom of nitrogen$=14$, and one atom of oxygen$=16$, and its formula is NO.

When 4 volumes of nitrogen dioxide are mixed with one volume of oxygen, the gases combine and form ruddy fumes, which have the composition N_2O_3, and the gas is called nitrogen trioxide. It can be prepared in quantity by heating starch and nitric acid, or still more conveniently by acting upon arsenic trioxide with nitric acid and warming the mixture.

$$\begin{array}{ccccccc}\text{Arsenic trioxide} & & \text{Nitric acid} & & \text{Water} & & \text{Arsenic acid} \\ As_2O_3 & + & 2(HNO_3) & + & 2(H_2O) & = & 2(H_3AsO_4) \\ & & & \text{Nitrogen trioxide.} & & & \\ & & & + \; N_2O_3. & & & \end{array}$$

It is a reddish brown gas which can be condensed to a dark greenish blue liquid at 18° C. At 0° C. water dissolves the trioxide without decomposing it, forming a blue liquid, which if heated is decomposed into nitrogen dioxide and nitric acid :—

$$\begin{array}{ccccccc}\text{Nitrogen trioxide} & & \text{Water} & & \text{Nitrogen dioxide} & & \text{Nitric acid.} \\ 3(N_2O_3) & + & H_2O & = & 4(NO) & + & 2(HNO_3). \end{array}$$

The blue solution formed with water at 0° C is supposed to contain nitrous acid :—

$$\begin{array}{ccccc}\text{Nitrogen trioxide} & & \text{Water} & & \text{Nitrous acid.} \\ N_2O_3 & + & H_2O & = & 2(HNO_2), \end{array}$$

and by the replacement of the hydrogen in HNO_2 by various metals, the class of salts called nitrites is produced :—

$$\begin{array}{ccccccc}\text{Sodic hydrate} & & \text{Nitrous acid} & & \text{Sodic nitrite} & & \text{Water.} \\ NaHO & + & HNO_2 & = & NaNO_2 & + & H_2O. \end{array}$$

When nitrogen trioxide comes in contact with free oxygen, it combines with it to form another reddish brown gas, nitrogen tetroxide which contains an atom more oxygen than the trioxide, and at low temperatures has the composition N_2O_4 ; but this undergoes complete dissociation at 140° C. into $2(NO_2)$ and NO_2 is therefore generally adopted as its molecular formula.

The gas can be obtained pure by heating lead nitrate, which breaks up into lead oxide, oxygen and nitrogen tetroxide.

$$\begin{array}{ccccccc}\text{Lead nitrate} & & \text{Lead oxide} & & \text{Nitrogen tetroxide} & & \text{Oxygen.} \\ 2[Pb(NO_3)_2] & = & 2(PbO) & + & 4(NO_2) & + & O_2. \end{array}$$

Nitrogen tetroxide forms colourless crystals at $-10°$ C., and these fuse to a colourless liquid which soon assumes a yellow colour, the tint increasing with the temperature up to 22° C., when the liquid is converted into a reddish brown vapour which continues to deepen in colour, until at 40° C. it is nearly black.

In ice cold water nitrogen tetroxide dissolves with formation of nitrous and nitric acids :—

Nitrogen tetroxide		Water		Nitrous acid		Nitric acid.
$2(NO_2)$	$+$	H_2O	$=$	HNO_2	$+$	HNO_3.

In water at ordinary temperatures it dissolves forming liquids which are blue, green or orange, according to the amount of the gas dissolved.

The gas (NO_2) may be heated to low redness without undergoing any actual decomposition.

Vigorously burning phosphorus and charcoal decompose it and burn with great energy, whilst potassium inflames spontaneously in the vapour and burns with a red flame.

The highest oxide of nitrogen—nitrogen pentoxide (N_2O_5)—was discovered, in 1849, by Deville, who prepared it by acting upon fused silver nitrate with dry chlorine.

Silver nitrate		Chlorine		Nitrogen pentoxide		Silver chloride		Oxygen.
$4(AgNO_3)$	$+$	$2Cl_2$	$=$	$2(N_2O_5)$	$+$	$4(AgCl)$	$+$	O_2.

It is a colourless solid, and forms prismatic crystals which melt at 30° C. ; when brought in contact with water it combines with it, with great evolution of heat, forming nitric acid :—

Nitrogen pentoxide		Water		Nitric Acid.
N_2O_5	$+$	H_2O	$=$	$2(HNO_3)$.

On an experimental scale nitric acid can be easily made from one of the more commonly occurring nitrates, such as potassic nitrate (saltpetre) or sodic nitrate (Chili saltpetre) by heating with concentrated sulphuric acid. Equal weights of dry potassic nitrate and concentrated sulphuric acid are mixed in the retort (Fig. 39) and gently heated, when nitric acid escapes as a vapour and is condensed to a yellowish liquid in the receiver which is kept cool by water dripping upon it.

Under these conditions and at a temperature to which a glass retort can be safely subjected, the reaction is represented by the equation :—

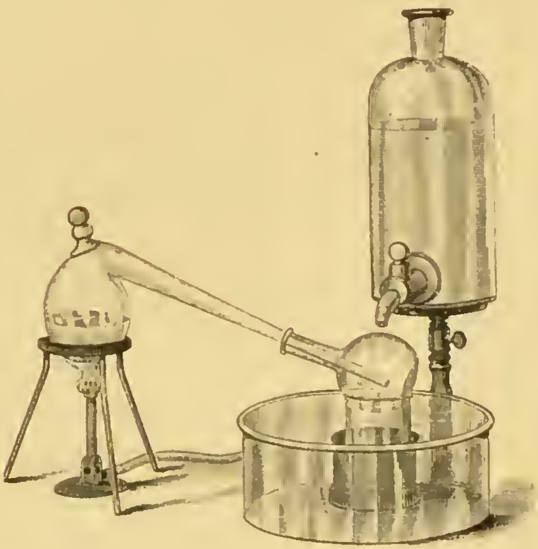


Fig. 39.

Potassic nitrate		Sulphuric acid		Acid potassic sulphate	Nitric acid.
KNO_3	$+$	H_2SO_4	$=$	$KHSO_4$	HNO_3.

That is to say, one half of the hydrogen present in the sulphuric acid is replaced by the metal potassium, whilst the hydrogen combines with the nitric acid radicle to form nitric acid. Nitric acid, when pure, is colourless ; but some is decomposed into nitrogen tetroxide, the ruddy fumes of which may be noticed in the retort, and which dissolving in the condensed acid colours it yellow.

When nitric acid is made on a commercial scale a much higher temperature is employed, and under these altered conditions the whole of the hydrogen of the sulphuric acid is replaced by two atoms of potassium; twice the amount of saltpetre being used for each part of the acid and double the quantity of nitric acid being formed.

Saltpetre.		Sulphuric acid		Potassic sulphate		Nitric acid.
$2(KNO_3)$	$+$	H_2SO_4	$=$	K_2SO_4	$+$	$2(HNO_3)$.

From this it is evident that in sulphuric acid one or both atoms of hydrogen can be replaced by a monad metal forming two distinct classes of salts; such as—

$KHSO_4$, acid potassic sulphate,
or K_2SO_4, normal potassic sulphate.

Hence sulphuric acid is said to be dibasic.

The hydrogen in nitric acid can only be replaced by potassium or sodium in one proportion, and it therefore is called a monobasic acid and only forms one class of salts.

Nitric acid so prepared has a specific gravity of 1.56 and is remarkable for its great oxidising power; it contains a very large proportion of oxygen, some of which it readily parts with, a property which its salts, the nitrates, also possess.

It will destroy the colour of indigo and stains the skin and other animal tissues a deep yellow; it converts many of the elements, both non-metallic and metallic into oxides, and is one of the most powerful agents for oxidising the lower metallic salts into higher compounds.

It has been shown that when an acid is brought into contact with a base, a salt is formed, and from the behaviour of sulphuric acid and potassic nitrate at different temperatures, it is evident that salts may vary in constitution with the temperature and the quantities interacting.

Salts which contain oxygen are classified as normal, acid and basic.

Normal salts are those in which all the replaceable hydrogen of the acid has been replaced by an equivalent weight of a metal or compound radicle, as—

$ZnSO_4$, zinc sulphate.
$(NH_4)_2SO_4$, ammonic sulphate.

Acid salts are those in which only a part of the hydrogen has been so replaced, as—

$KHSO_4$, acid potassic sulphate.
$NH_4H_2PO_4$, ammonic dihydric phosphate,

whilst basic salts contain a certain proportion of the oxide or hydrate of the metal.

$2(PbCO_3)\ Pb(HO)_2$ basic lead carbonate.

The fact of a salt having an acid or alkaline reaction to test papers cannot be taken as any indication of the class to which it belongs, as the combination of a strong base with a feeble acid often yields a salt having an alkaline reaction, whilst many normal metallic salts give acid reactions with blue litmus paper.

When nitric acid is added to metallic copper a colourless gas is given off which instantly becomes ruddy brown on coming in contact with the air, and this reaction constitutes a test for the acid. If, however, the nitrate is present as a salt, it is necessary to liberate the acid by warming with excess of hydric sulphate.

When the nitrate is only present in very small traces a still more delicate test is necessary.

An equal bulk of strong sulphuric acid is added to the solution supposed to contain the nitrate. The mixture is then cooled and a solution of ferrous sulphate is carefully poured on to the surface of the mixture, and if a nitrate is present a brown ring forms at the junction of the two liquids.

CHAPTER XII.

THE ATMOSPHERE.

The extent of the atmosphere—Weight of the atmosphere—The barometer—Composition of the atmosphere—Air a mechanical mixture and not a chemical compound—Gases other than oxygen and nitrogen present in the atmosphere—Ammonia, water vapour, carbon dioxide—The natural actions which keep the composition of the atmosphere constant—Solid, liquid, and gaseous impurities present in the atmosphere.

THE air in which we live and breathe is essentially a mixture of the two elementary gases nitrogen and oxygen, containing also small quantities of carbon dioxide, water vapour and ammonia, which are always present—and have special functions to perform with regard to the economy of Nature—and is also charged with all the gaseous impurities formed both naturally and artificially on the earth's surface.

The atmosphere forms a gaseous layer surrounding the earth, and, according to calculations made by Wollaston, based upon the duration of twilight, it extends about forty-five miles above the surface of the earth; whilst other observers, basing their calculations upon purely mathematical data, urge that there is no such limit, and that the atmosphere extends through space. It is well known, however, that the density of the atmosphere rapidly diminishes as we ascend from the earth's surface, and that at an elevation of three and a half miles its density is reduced to one half that of the sea level.

The fact that the air has weight, and is therefore exerting a pressure upon all objects was not proved until the middle of the seventeenth century, when Torricelli, in trying to find an explanation of the fact that a pump would only raise water a little over thirty two feet, discovered that if water were enclosed in a tube which dipped into a reservoir of water open to the air, and if there were a perfect vacuum in the upper portions of the tube, ~~that~~ the water would stand at a height of thirty three feet; whereas, under the same conditions, mercury only stood at a height of 30 inches. On determining the relative weights of mercury and water, he at once found that if he employed tubes of equal diameter, the column of mercury 30 inches in height weighed the same as the column of water 33 feet in height; and from this he concluded that there must be some natural sustaining force of which this weight of mercury or water was a measure, and after searching for a cause, he finally came to the conclusion that it must be the pressure of the atmosphere which was balancing the columns of liquids; a conclusion which was verified by Blaise Pascal, in 1648, taking Torricelli's tubes up a high mountain, when he found that as he ascended and the amount of atmosphere above his instruments decreased, so the height of the liquid columns was diminished.

If a large glass U tube is taken, each arm of which is 33 inches long and open at each end, and if into this mercury is placed, the mercury will stand level in each arm of the tube (A, Fig. 40), but if now one end is closed and is then completely filled with mercury, on replacing the tube in position, the mercury will only fall in the tube until the difference between the levels of the mercury is 30 inches (B, Fig. 40), that is to say, the pressure of the atmosphere on the surface of the mercury in the open tube is able to balance a column of 30 inches of mercury in the closed arm of the tube with no air above it. The vacuum left in the closed arm of the tube is called after-its discoverer the "Torricellian vacuum." Torricelli's tube was afterwards named by Boyle the "Barometer," and it is the instrument in general use for measuring the pressure of the atmosphere; if in the experiment with the U tube, a tube had been chosen having a sectional area of one square inch, the atmospheric pressure on the square inch of mercury exposed, would have been equal to the weight of the column of mercury supported, *i.e.*, 30 cubic inches and this amount weighs 15 lb., so that the pressure of the atmosphere is said to be 15 lb. on the square inch.

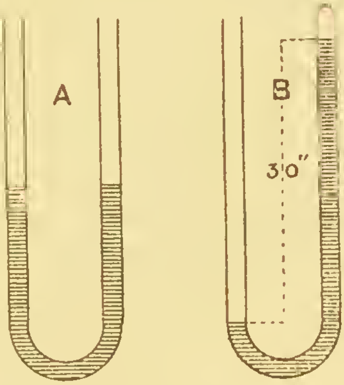


Fig. 40.

The effect upon the height of the mercurial barometer exerted by the pressure of the air can easily be shown by placing a barometer tube under the receiver of an air pump, when each stroke of the pump will cause a corresponding fall in the column of mercury.

29.96 inches is equivalent to 760 millimeters, which is taken as the normal height of the barometric column in all scientific work, whilst the pressure exerted by the atmosphere would be expressed in the metrical system as 1.03296 kilograms on a square centimeter.

The pressure of 15 lb. on the square inch is taken as the pressure of one atmosphere and pressures are often expressed in this way; if for instance the pressure of steam in a boiler was equal to 60 lb., it would be said to exert a pressure of four atmospheres.

If taking 15 lb. on the square inch, we calculate the pressure exerted on any extended surface, it is found to be very considerable, an ordinary sized man sustaining a pressure of nearly 16 tons on the surface of his body, which, however, is so delicately balanced that he is perfectly unaware of its existence.

If water is boiled for some time in a circular tin bottle, the escaping steam drives all air out of the vessel, and being itself at the same pressure as the atmosphere balances it; if, however, the tin be corked air tight whilst still full of steam, and cold water is thrown over the vessel, the steam is condensed and the vessel being unable to withstand the external pressure of the atmosphere is at once crushed.

Air is not a chemical compound, but a mechanical mixture of the two elements oxygen and nitrogen.

Percentage composition of air:—

	By weight.	By volume.
Nitrogen	76.9	79.1
Oxygen	23.1	20.9

or roughly, 4 volumes of nitrogen to each volume of oxygen.

During the years 1774-75 oxygen gas was discovered independently by Priestley in England and Scheele in Sweden, and three years later the great French chemist Lavoisier discovered and pointed out the functions of oxygen and the part played by it in all cases of combustion in air—a discovery which is by many considered to be the birth of modern Chemistry.

It has been shown (page 9) that a mechanical mixture retains the properties of the substances forming it, and we have in it the component parts merely lying side by side in a state of physical mixture; in a chemical compound, on the other hand, we have all the properties of its components merged and new properties developed which are characteristic of the compound formed.

The reasons for considering air to be a mixture and not a compound are as follows:

1. If we bring oxygen and nitrogen together in the proportions in which they occur in air, there is no elevation of temperature or alteration in volume, and yet the mixture has all the properties of air.
2. The relative quantities of the two gases present are not those of their combining weights, nor of any simple multiples of these weights.
3. When air is shaken up with a small quantity of water, some of it is dissolved, and if this dissolved air be expelled from the water by boiling, it is found to consist of oxygen and nitrogen, in the proportions of 1 to 1.87, and not 1 to 4. Now had air been a chemical compound it would have dissolved as a whole, and on being expelled from solution the oxygen and nitrogen in the original proportion of 1 to 4 would still be maintained.
4. The proportions in which the two gases occur occasionally vary slightly.
5. Nitric oxide forms ruddy fumes in contact with air, showing that the oxygen present is uncombined.

The volumetric composition of air is best determined by means of the eudiometer, the same method being employed as in the volumetric synthesis of water, the only difference being, that instead of experimenting with pure oxygen we use air, and having passed up excess of hydrogen, we explode the mixture and notice the diminution of volume. Now we know that two volumes of hydrogen combine with exactly one volume of oxygen to form water; hence one-third of the observed diminution in volume must represent the oxygen which has disappeared and therefore the volume of oxygen in the air taken. The amount of oxygen by weight in air is determined by passing a known volume of purified air slowly over red hot copper turnings in a hard glass tube; the copper takes all the oxygen from the air, forming cupric oxide, and by carefully weighing the tube of copper before and after the experiment, the increase in weight—due to the oxygen in the volume of air taken—is determined.

Air being a mechanical mixture and having the properties of its constituents, it is at once evident that oxygen is the great supporter of life and combustion, whilst the function of the nitrogen is to dilute it and keep its action within the proper limits. This fact having been established by Priestley and Lavoisier, it was imagined that the great secret of health had been discovered and that air was wholesome in proportion to the amount of oxygen it contained; but of late years this theory has been exploded by the fact that the variation in the percentage of oxygen in good and bad air is very slight. In a long series of analyses made by Angus Smith, of samples of air, the extreme variations are 20.99 per cent. in a sample of air from the Scotch Moors, and 20.63 per cent. in air collected in the gallery of a London theatre towards the close of the performance.

Volume for volume air is 14.47 times as heavy as hydrogen.

Besides oxygen and nitrogen there are three other important gaseous bodies present in air, water vapour, carbon dioxide and ammonia, which have important parts to play in natural processes and must not therefore be looked upon as impurities until the amount exceeds a certain limit.

AVERAGE COMPOSITION OF THE ATMOSPHERE.

Oxygen	20.61
Nitrogen	77.95
Carbon dioxide	0.04
Aqueous vapour	1.40
Nitric acid Ammonia	traces
	100.00

Ammonia is present in very small traces, but is of great importance to vegetable life, as it is from this gas that plants obtain a large proportion of the nitrogen which they require to form their seeds and fruit. It is evident that ammonia could not be present in large quantities in the air unnoticed on account of its pungent odour, its great solubility enables every shower that falls to collect it from the air and bring it down to the vegetation which needs it.

Water vapour is present in varying quantities dependent chiefly upon the temperature. The warmer the air the more water it can hold in suspension as vapour; when warm air is cooled by coming in contact with colder layers of air, it cannot any longer hold so much moisture, and deposits the surplus as rain. In the night time, while the surface of the ground is receiving no heat from the sun, it is constantly losing heat by radiation, and on a clear night soon becomes colder than the air above it, and the lower strata of air are then cooled by contact with it, causing a condensation of moisture in the form of dew.

Water vapour in the air has an enormous influence upon our comfort and health. The human body is largely composed of water, and if the air becomes too dry, evaporation from the skin and lungs is increased, causing great discomfort.

The aqueous vapour in the atmosphere also plays an important part in warming the air, as the vapour contains a large amount of latent heat which is given up to the air during condensation, besides which its presence retards the passage of heat rays through the air and so raises the atmospheric temperature.

When animals or human beings breathe, the life supporting principle of the air is exchanged for carbon dioxide, which by this process is continually being poured into the atmosphere, and this gas is also formed during all processes of combustion, whether they be rapid, as when wood is burnt in a fire, or slow, as when vegetable matter rots away. It is also produced by processes of fermentation, and escapes in enormous quantities into the atmosphere from the earth, from natural sources.

It must be remembered that during most processes which give rise to carbon dioxide, oxygen is being absorbed, and it has been computed that this takes place at the rate of over three and a half millions tons per diem—a rate which would rapidly diminish the percentage of oxygen and increase that of carbon dioxide, the air being rendered unfit to support animal life.

It has, however, been shown by the researches of Fruchot, Schultze and others, that in the open air the percentage of carbon dioxide varies but little, the average amount being 4 volumes in 10,000 of air—this quantity decreasing after rain and increasing during frost and fog and at night time, but again diminishing after sunrise; it is therefore evident that there is some natural agency at work which tends to neutralise the effects of animal life and decay, and it is found that vegetable life plays an important part in this process of purification.

If the leaves of any form of vegetation be examined, they will be found to be covered with minute funnel shaped pores which are in connection with small cells containing a green matter called "chlorophyll," which gives the colour to vegetation.

Under the influence of the sun's rays the growing plant absorbs carbon dioxide from the air through the pores in the leaves, and it is then decomposed by the chlorophyll, the carbon being mostly assimilated by the plant to form its woody fibre and so carry on its growth, whilst the oxygen is once more returned to the air, tending to keep it in a condition fit for respiration.

This wonderful process would, however, be of little use by itself, as in large towns and manufacturing districts where enormous amounts of carbon dioxide are formed, there is, as a rule, but little vegetation and still less sunshine, so that the gas would accumulate and seriously impair the purity of the air were it not that the diffusion of gases, aided by the winds and air currents, tends to mix all the constituents of the atmosphere evenly together, and where sunshine and vegetation exist, there the carbon dioxide is decomposed, and the oxygen once more spread throughout the air by diffusion, and thus a practically constant proportion is maintained.

Were it not for the action of gaseous diffusion the constituents of the atmosphere would arrange themselves in layers according to their densities, and life would be an impossibility.

When we breathe, the exhalations from our lungs contain not only carbon dioxide but also water vapour. If we breathe into a glass jar for 24 hours, keeping it cold so as to condense the water vapour, it is found that nearly a pint of water is condensed in the jar, and if this be allowed to stand for a few days, or even hours, it will putrefy and become offensive, showing that besides water there is present organic matter, and it is this organic matter which is accompanied by the germs of disease and is one of another class of impurities which are to be found in the atmosphere, and which are purely local and have local causes, and which perhaps affect health more than anything else.

These are—First, suspended solids, which we find floating in the air as dust, partly mineral substances which induce certain diseases from the merely mechanical effect of local irritation; and partly organic bodies, such as the germs of infusoria, fungi, etc., which have come into great prominence during the last few years from the investigations of Schrœder, Davaine, and Pasteur, and which at the present moment are the favourite explanation of the spread of many kinds of disease.

Secondly, suspended liquids, such as the fog formed by partly condensed water vapour, which, by keeping down the smoke and solid impurities, irritate and affect respiratory organs and eyes ; and Thirdly, gases, such as sulphur dioxide and sulphuretted hydrogen in volcanic districts, hydrochloric acid and chlorine in manufacturing districts, and marsh gas on bog lands, these gases having a greater effect on vegetation than on human beings.

These impurities all have prejudicial effects upon health and life, but it is the effect of several impurities acting together which most ordinarily affects us ; for instance, 4 volumes of carbon dioxide in 10,000 of air is the normal quantity, whilst 50 in 1,000 prove fatal to life and 15 to 20 cause severe headache, yet in the act of respiration headache and giddiness are produced when the amount of carbon dioxide is not more than 1.5 volume in 1,000 ; but then organic matter is present as well and exerts a very considerable influence upon the functions of the body.

Air which has been once breathed contains nearly 5 per cent. of carbon dioxide, and is totally unfit to be again drawn into the lungs as the rate of interchange between carbon dioxide and oxygen is disturbed ; dark venous blood is distributed through the system instead of being converted into red arterial blood, and death is ultimately caused by suffocation.

Rain assists in purifying air, by dissolving soluble gases such as ammonia and carbon dioxide, and washing the atmosphere from germs and dust. The oxygen in the atmosphere, in the presence of moisture has the power of slowly oxidising or burning away organic matter ; a heap of dead leaves or wood slowly is converted into carbon dioxide and water, a dead animal slowly disappears with certain changes in its composition, and a still more active agent in thus keeping the face of the earth free from impurities is the modification of oxygen known as ozone.

When we are in the open air, these provisions of Nature are ample to maintain the air in a fit condition for breathing; but when we are in an enclosed space, such as a room, then it is necessary to provide means to help Nature carry out her processes, or else we rapidly contaminate the air to a point at which it becomes unfit for respiration.

CHAPTER XIII.

VENTILATION.

Amount of air required for respiration—Air space—Air currents—Effect of various methods of heating upon ventilation—Open fires—Closed grates, hot air, steam—Vitiation of the atmosphere by illuminants——Candles, oil lamps, gas burners—Relative effects of various types of burners—Incomplete combustion—Gas as a ventilating agent—Heat evolved by illuminants—Ventilation of ships—Objections to forced draught.

THE average amount of carbon dioxide in the outer air is 4 parts in 10,000, and experiment has shown that whenever the amount of carbon dioxide in the air of a room exceeded the amount in the open air by more than 2 parts per 10,000, then the air of the room was not fresh and had a stuffy smell owing to the organic matter and moisture present; hence 6 parts per 10,000 are fixed as the limit of impurity.

An adult breathes out about six cubic feet of carbon dioxide gas in ten hours, and therefore in order that the air of the room he is in may be kept fresh, it is evident he must be supplied with 30,000 cubic feet of air in ten hours, or 3,000 in one hour. A person inhabiting a bed room for seven hours would require 21,000 cubic feet of air, and if no means were provided for changing the air of the room, it would have to be 70 feet long by 30 feet wide by 10 feet high. It is clear that we cannot have rooms of this size, and therefore in the rooms we use there must be a change of air, and this is obtained by the process called ventilation. We cannot change all the air in a room more than three or four times in an hour without creating a draught, and so for each person should be allowed from 1,000 to 750 cubic feet of space, the air of which should be changed three or four times in the hour, thus providing the requisite amount of fresh air.

In ventilation, attention should be paid to the following points: (1) The air which enters should be pure; (2) Its movement should be imperceptible, otherwise it causes what we call a draught and sensation of chill; (3) The incoming air must be evenly distributed through the room, so that every part shall be undergoing change; (4) The air should be removed so quickly that there is no risk of the same air being breathed more than once.

The means by which air is set in motion for purposes of ventilation may be natural or artificial; in nature, the causes at work are, diffusion, wind, and the differences in weight between unequally heated masses of air. Air diffuses with great rapidity through chinks and openings due to bad carpentry, and also through bricks and walls built of porous materials. The amount of purification effected by diffusion is, however, insufficient.

Wind acts as a powerful ventilating agent. If it can pass freely through a room with open doors and windows, at a rate of two miles an hour, which is almost imperceptible, if the room is 20 feet wide, it will change the air of the room 528 times in one hour. Air is called "still" when in reality it is moving a mile or a mile and a-half per hour. The average movement of air in England is six to eight miles per hour.

Wind is caused by the air in certain places becoming heated, when it expands, becomes lighter than the surrounding atmosphere, and ascends, cool air rushing in to take its place.

When any gas, measured at a temperature of 0° C., is heated, it expands $\frac{1}{273}$ of its bulk for each degree centigrade, so that supposing we had a cubic foot of air measured at 0° C., at 273° C. it would have doubled its volume, and each cubic foot of the expanded air would weigh half as much as the original air. From this it is evident that in an enclosed space, such as a room, the impure air after respiration or combustion has been carried on, being at a higher temperature, will rise, and that therefore the impure air in a room is to be found near the ceiling.

Expansion from heat is not the only cause of air rising and thus forming currents; water vapour is lighter than air, hence when air contains much water vapour in suspension it is lighter than dry air, and ascends.

From these facts it will be seen that the methods employed in heating and lighting a house not only play an important part in deteriorating the quality of air by removing oxygen and giving back to the air carbonic acid, but they also may be made important factors in the ventilation owing to the tendency to upward movement produced in the foul air by rise of temperature, and moisture formed during combustion; and one of the most ordinary forms of ventilation consists in making openings near the top of the room, leading either into the flue or into the open air, whilst corresponding openings are arranged near the floor for the admission of fresh air.

The method generally adopted for warming rooms is, in England, the open fire place—perhaps the most comfortable and most wasteful that could be adopted. If a pound of coal could be burnt, and all its heat of combustion utilised in heating a room 20 feet square and 12 feet high, it would be more than sufficient to raise the temperature of the room ten degrees above the temperature of the outside air, and if there were no ventilation, and the walls were non-conductors of heat, the amount of fuel required to keep up this temperature would be very small; as it is, in an ordinary grate the consumption averages eight pounds per hour; but this consumption of fuel enables the open fire to perform other functions besides those of heating, and it may be said to be the great engine of ventilation.

One pound of coal requires for its complete combustion about 160 cubic feet of air, and the eight pounds would require 1,280 cubic feet; but at a very low computation of the velocity of the gases in an ordinary chimney flue, the air would pass up at a rate of from four to six feet per second, or 14,000 to 20,000 cubic feet per hour, while with a velocity of 10 to 15 feet per second, which is often attained, the flow of air would be 35,000 to 40,000 cubic feet per hour; and all this volume of air which passes out of the room is warm and carries heat away with it, whilst the fresh air which takes its place is cold, and lowers the temperature of the room. Another drawback is that this great volume of air drawn out by the chimney has to be replaced, and the fresh air rushing in through crevices and other small openings gives rise to draughts.

When an open fire burns, the radiant heat from it does not directly warm the air of the room, but the fire heats the back, bars and sides of the grate, and these in turn radiate heat to the walls and ceiling of the room, which in turn warm the air in contact with them. A good fireplace should, for this reason, have its sides and back made of a bad conductor of heat, but a good radiator, thus bricks or tiles are better for this purpose than iron.

The normal temperature of the human body is 98° F. or 36.8° C., and this temperature is maintained by a continuous process of combustion going on in our bodies, which are continually giving off a certain amount of heat. According to the laws of radiation, any heated substance parts with its heat more or less rapidly according to the temperature of the surrounding bodies, so that if a person is sitting in a room full of warm air, but near a wall that is colder than the air, his body rapidly loses heat by radiation to the wall, and a sensation of chill is experienced; with an open fire this is never the case, as the radiation from the fire heats the walls of the room to a higher temperature than the air; but when a room is heated by means of hot water pipes or by means of warmed air, the walls are not heated in the same proportion, and although the air may feel warm the walls may remain cold, so that the heat of the body may pass by radiation to the walls and give rise to a sensation of chill.

It is much more healthful to breathe cool than hot air, as bulk for bulk it contains more oxygen.

If the open fire is done away with, it has to be replaced either by closed slow combustion stoves, by heating by warmed air, by hot water, by steam, or by gas. In slow combustion stoves, a much larger amount of heat is obtained per pound of fuel consumed, but they have several drawbacks, such as allowing carbon monoxide and other injurious products of combustion to escape into the air, and should only be used in lobbies or galleries where there is ample ventilation.

In heating by air, cold air may be raised to a certain temperature by passing over heated surfaces and can then be discharged into the building to be warmed, the drawbacks to this system being that the air is generally warmer than the walls, and also that it does not allow of any one room being made hotter or cooler than the rest. In warming by hot water pipes, the water is heated to a given temperature in a central boiler and is then made to circulate through iron tubes in the chambers to be heated; this system is, of course, open to the same objections as the last.

In the United States, heating by steam is the most generally adopted plan. The steam is conveyed from the basement by means of pipes to the room or passage in which it is to be used, and there it is passed into a coil of pipes, called a radiator, which gives an increased heating surface; here the steam gives up some of its heat and becomes condensed to water, forming a partial vacuum in the tubes and sucking up fresh steam to take its place, the condensed water flowing back once more to the boiler and being converted into steam. The difficulty in steam heating is to regulate the temperature of the pipes, as the temperature rises very rapidly when the steam is turned on and falls as rapidly when turned off.

There is a great prejudice against heating by steam in England, as for some reason it is not considered safe. Of late years gas has come largely into use as a warming and ventilating agent, and can be either applied to open fireplaces, where a large atmospheric burner is made to heat asbestos, which in turn radiates out heat to the room, or it is used to heat a current of fresh air or a small service of hot water pipes.

The subject of lighting is so intimately connected with that of heating and ventilation that it is impossible to pass away from these subjects without taking it into consideration.

The sources from which we obtain artificial light are: candles, lamps consuming oils, coal gas, and arc and incandescent electric lamps.

Taking these sources of light in their historical order, we come first to oil, then to candles, and finally to gas. If we examine the composition of the light giving waxes, fats, oils and gases, we shall find that in each case the constituents upon which they depend for their lighting and heating powers are the elements carbon and hydrogen, which by a selective process of combustion, emit light; and in each case the chief products of combustion, when it is complete, are water vapour and carbon dioxide, together with minute quantities of other gases, either formed from impurities in the illuminants or from incomplete combustion, which latter also gives rise to the small particles of carbon which blacken ceilings.

The unit of illuminating power adopted in England is a sperm candle of the size known as "sixes," which, when burning under normal conditions, consumes 120 grains of sperm per hour, and gives a light known as "1-candle power;" and as it is convenient to quote the amount of carbon dioxide and water vapour given off from the various illuminants per candle power of illumination, it will be convenient, for purposes of comparison, to consider the sperm candle as the type in general use. The substances of which these candles are composed show on analysis the following composition :—

	Per cent.
Carbon	80.0
Hydrogen	13.3
Oxygen	6.6
	99.9

On complete combustion in air, 120 grains yield 0.41 cubic foot of carbon dioxide, and the same volume of water vapour; or in other words, these volumes of carbon dioxide and water vapour are given off in an hour for every candle power of illumination derived from sperm candles.

Many kinds of oil have been used for illuminating purposes; but the only one which, from its cheapness and illuminating power, has ever threatened the popularity of gas is petroleum, paraffin, or mineral oil; of late years this has been obtained in such increasing quantities that it bids fair to become of paramount importance among the illuminating and heating agents of the future. On analysis the average composition of paraffin oil approximates to :—

	Per cent.
Carbon	86
Hydrogen	14
	100

The average consumption per candle power is about 62 grains per hour when burnt in the newest forms of lamps; and the volumes of carbon dioxide and water vapour produced by the combustion of this amount of the oil are respectively 0.28 and 0.22 cubic foot.

Coal gas consists of a mixture of several gases derived from the destructive distillation of coal, and varying considerably with the class of coal used, and also with the processes employed in its manufacture and purification. Ever since the first introduction of coal gas as an illuminating agent, steady progress has been made in its production and purification; and the quality and purity of the London supply at the present time leaves little to be desired. Taking the gas as supplied to the City and to London, north and south of the Thames, the average composition is:—

	Per cent.
Hydrogen	49.54
Methane	36.64
Ethylene or similar hydrocarbons ...	5.78
Carbon monoxide...	4.06
Carbon dioxide	0.03
Nitrogen	3.71
Oxygen	0.24
	100.00

Every cubic foot of this gas consumed yields 0.52 cubic foot of carbon dioxide, and 1.34 cubic feet of water vapour; whilst the illuminating power per cubic foot depends upon the burner which is used in its consumption. The various forms of burner have been fully discussed under the subject of coal gas, and selecting the best burner of each class for photometric comparison and experiment, the following results are obtained:—

Type of Burner.	Illuminating power per cubic foot of Gas consumed. Candles.	Products of combustion per candle power.	
		Carbon dioxide. Cub. ft.	Water vapour. Cub. ft.
Batswing	2.9	0.18	0.46
Argand	3.3	0.16	0.40
Incandescent	6.0	0.09	0.22
Regenerative	10.0	0.05	0.13

These figures are obtained by testing the burners with gas of the composition supplied by the London Gas Companies. Taking now the amount of the products of combustion given off per candle of illuminating power, it is possible to arrive at the relative vitiating effect which the various sources of illumination produce on the air of a dwelling room, and to compare these results with the effect produced by respiration. It has been found by experiment that an adult exhales 0.6 cubic foot of carbon dioxide per hour; and also that, as the percentage of organic impurities in the air of a room increases with the rise in quantity of carbon dioxide, the amount of carbon dioxide present may be taken as an index of the sanitary condition of the atmosphere, and it has been shown that an adult exhaling 0.6 cubic foot of carbon dioxide per hour will require 3,000 cubic feet of air space for healthy respiration. But, inasmuch as diffusion through the walls and crevices in door and window frames, and ventilation by the chimney, changes the air of a room at least three times in an hour, 1,000 cubic feet of air space has been decided upon as the allowance per adult in rooms which are to be continuously used as dwelling apartments. Taking now a small sized room—say, 12 ft. by 16 ft. by 10 ft.—it would not be considered properly illuminated unless the light were at least equal to 32 candle power. In the following table is given the amount of oxygen used up, and products of combustion formed, by each class of illuminant and burner, in order to secure this result; and the amount of carbon dioxide so formed is also expressed in the number of adults who would exhale the same amount during respiration:—

Amount of Oxygen removed from the Air, and Carbon dioxide and Water Vapour generated to give an Illumination equal to 32 Candle Power.

Illuminant.	Quantity burnt.	Oxygen removed.	Products of Combustion.		
			Water vapour.	Carbon dioxide.	Equal to adults.
	Grains.	Cub. ft.	Cub. ft.	Cub. ft.	
Sperm candles	3,480	19.27	13.12	13.12	21.8
Paraffin oil ...	1,984	12.48	7.04	8.96	14.9
Gas (London)—					
Burners:	Cub. ft.				
Batswing ...	11.0	13.06	14.72	5.76	9.6
Argand ...	9.7	11.52	12.80	5.12	8.5
Incandescent ...	5.3	6.30	7.10	2.75	4.6
Regenerative ...	3.2	3.68	4.16	1.60	2.6

From these data it would appear that, according to the rules laid down in sanitary science, by which the degree of vitiation of the air of any confined space is measured by the amount of oxygen used up and carbon dioxide formed, candles are most prejudicial to health and comfort, oil lamps less so, and gas least—an assumption which practical experience does not bear out; the discomfort and oppression felt being distinctly less in a room lighted by candles or oil than in one lighted by any of the older forms of gas burner. The explanation of this is to be found in these facts: First, that where we illuminate a room with candles or oil, we are contented with less intense and more local light than when we are using gas; and in a room of the size described, should be more likely to use two candles, placed near our book or plate, than thirty two scattered about the room. Secondly, because the amount of water vapour given off during the combustion of gas is greater than in the case of the other illuminants, and water vapour absorbing radiant heat from the burning gas, becomes heated, and, diffusing itself about the room, causes great oppression. Also the air, being highly charged with moisture, is unable to take up so rapidly the water vapour which is always evaporating from the surface of our skin; and in this way the functions of the body receive a slight check resulting in a feeling of "malaise." Further, in burning coal gas, if the gas be pure and combustion perfect, the products may be looked upon as carbon dioxide and water vapour only; but in all gas we find small quantities of sulphur compounds—even the highly purified London gas containing 10 to 13 grains of sulphur per 100 cubic feet in the form of bisulphide of carbon vapour. This sulphur, during the combustion of the gas, burns to sulphurous acid, which, if it were present in any considerable quantity, would not only be injurious to health, but also destructive to furniture, drapery, books, &c., exposed to it, because, when in the presence of moisture and air, it is oxidised to sulphuric acid. But when the smallness of the trace present in London gas is considered, and the enormous volume of air with which the sulphur dioxide is mixed, and that only a small percentage of this again will be oxidised in the room to sulphuric acid, it must be admitted that it is unreasonable to hold it responsible for all the mischief laid to its account.

A much more serious evil, however, does exist in the products of incomplete combustion of coal gas—viz., carbon monoxide and acetylene, which, even in small traces, seriously affect health. Whenever carbon escapes unburnt from a flame, there incomplete combustion is going on; and considering how impossible it is to employ an uncovered burner of any type without quickly blackening the ceiling, it is realised how universal this incomplete combustion is. Finally, when we use gas, the hot products of combustion collect next the ceiling, the emanations from the body and expired air being at a lower temperature than the products of combustion, do not rise through them; so that practically as far as ventilation is concerned, the ceiling is lowered to the level of the gas burners.

All these considerations lead to the conviction that, for health, adequate ventilation is essential, no matter what source of illumination is employed, electric lighting being excepted. If candles or oil are used, all that can be done is to secure the ventilation of the room by the ordinary methods, as the conditions under which these sources of light are employed prevent use being made of them as ventilating agents. But with gas this is not the case. When coal gas was first employed in the early part of this century, as an illuminating agent, the low pitch of the old fashioned rooms, and the excess of impurities in the gas, rendered it imperative that the products of combustion of the sulphur laden gas should be conducted from the apartment; and for this purpose arrangements of tubes with funnel shaped openings were suspended over the burners, and led away the noxious gases either to the flue or the open air. This type of ventilation, however, was unsightly in the extreme; and some few attempts were made to replace it by a more elegant arrangement, as in the ventilating lamp invented by Faraday. But with the advance of the gas industry, the methods for purifying coal gas became gradually more and more perfect; whilst the rooms in modern houses increased in height, and the products of combustion became mixed with a larger volume of air, thus became if not much less noxious, at all events much less offensive to the nose. As soon as this point was reached, the ventilating tubes were discarded; and from that day to this the air of our dwelling rooms has been contaminated by illuminants with hardly an effort to improve its condition.

In places of public entertainment where large quantities of coal gas are consumed for illuminating purposes, the absolute necessity for special ventilation gave rise to the "Sun burner" with its ventilating shaft, which however gives but a very poor illuminating power per cubic foot of gas consumed, due partly to the cooling of the flame by the current of air produced, and partly to its distance from the objects to be illuminated.

The great obstacle which in the history of ventilation has opposed itself to the adoption of proper arrangements for removing the products of combustion, has been the necessity of bringing the tube to carry off the gases low down into the room, and of encasing the burner in such a way that none of the products should escape. But with the present revolution in burners, this necessity is entirely obviated; and the regenerative burner gives the means, not only of removing all the products of combustion, but also of effecting a thorough ventilation of the room itself.

In order to convert a regenerative gas lamp into an efficient ventilating agent, it is enclosed in a metal case, which is enlarged and ornamented at the bottom to form a centre piece to the ceiling, and through the case perforations communicate with the room; whilst the upper part of the metal case or air box is sunk into the ceiling space, and is surrounded by an outer casing—the space (1½ inch) between the two being packed with silicate wool, which, being a non-conductor of heat and perfectly incombustible, keeps the outer casing from rising above a temperature of from 78° to 100° F. This air box, which contains the regenerative portion of the burner, is connected by a cased tube, carried through the ceiling space to a shaft passing either up the flue or to an external shaft; and up this the heated products of combustion pass, causing a brisk draught, thus are removed not only the combustion products, but also the heated impure air from the upper part of the room.

The heating effect produced by illuminants and the action this has upon the atmosphere must now be considered. A luminous flame, whether it be from a candle, oil, or gas burnt in ordinary incandescent or regenerative burners, heats the air and surrounding objects in two distinct ways—(1) By convection; the hot products of combustion mixing with the cool air, and producing currents by which gradually the temperature of the whole mass of air present becomes raised. (2) By radiation from the incandescent particles of ignited carbon in the flame, which latter does not directly heat the air but passes through it, heating the solid bodies with which it comes in contact, and also the water vapour present in the air.

Now, the kind of heat emitted by a gas flame depends entirely upon the conditions under which it is burning, the amount of solid matter in the flame capable of being heated to incandescence, and the temperature to which this solid matter is heated. This may best be seen by burning a mixture of gas and air, as in the Bunsen burner, which gives a non-luminous flame, and but little radiant heat, but which will quickly warm the air by convection. If a coil of platinum wire is held in the flame, it becomes heated to incandescence, and gives out both light and radiant heat; and these are produced at the expense of the heat of combustion, which before expended itself in heating the products of combustion and the surrounding air. In an ordinary illuminating flame (whether from gas, candles, or oil), solid particles of carbon are present, which, being heated to incandescence, emit light and radiant heat; their liberation in each case being due to a selective combustion of hydrogen and carbon. The hydrogen, having a greater affinity for the oxygen of the atmosphere, burns first; and the carbon liberated for a moment is heated by the burning hydrogen to the point at which it emits light. The amount of light evolved depends entirely upon the temperature—the higher the solid particles can be heated, the more light is evolved. In the regenerative burners the heat of combustion is utilised to heat these carbon particles to the highest possible temperature, and so to extract from them the largest amount of light; and in so doing a certain proportion of the heat of combustion is translated into radiant heat.

In order to ascertain the amount of radiant heat emitted, a small ventilating burner was fixed in a room 12 ft. by 15 ft. by 10 ft., the average temperature of which was 66° Fahr., and thermometers were arranged vertically below the burner at distances of 12, 18, 24, 36, 48 and 60 inches, with these results—

Distance below Flame. Inches.	Degrees Fahrenheit.	Degrees Centigrade.
12	78.8	26.0
18	70.6	21.5
24	68.9	20.5
36	68.0	20.0
48	67.1	19.5
60	66.2	19.0

Therefore at a distance of 5 feet below the flame, the radiant heat only caused an increase of temperature of 0.2° F. above the ordinary temperature of the room; and this increase can be avoided by suspending a sheet of glass a few inches below the shade of the burner, which although it allows about 88 per cent. of the light to pass through, stops the radiant heat.

In the ventilation of ships it must be remembered that the important factor of diffusion through the wall space is entirely eliminated, and that it is therefore necessary to pay all the more attention to artificial ventilation, a subject which has received but scant attention in the Navy, owing to the structural difficulties which have to be contended with, and which do not exist in the fast ocean steamers and mercantile marine.

In the older boiler and furnace arrangements, burning with natural draught, the stokeholds and engine rooms were practically open, whilst the other portions of the ship were in connection by means of air tubes with canvas cowls, which, whilst the vessel was in motion, kept up a constant air supply. With the introduction of the forced draught, however, a change had to be made, as it was not considered desirable to feed the draught directly to the fire boxes, as is done in most of the fast liners, but to make the stokehold as air tight as possible, and to feed warm air into it by means of fans, so as to make it an air reservoir, with a pressure in it equal to an inch or an inch and a half of water, with practically the only outlet through the furnace ; this arrangement being considered necessary, in order that when the vessel was not required to go full speed, natural draughts could be used by opening up traps over the stokehold, whilst, when great speed was required, the stokehold was battened down and the pressure of air obtained by the use of the fans.

The great objection to this is that the outlet for the air is at the bottom of the stokehold, whilst the hot foul air accumulates above, and being under pressure leaks out into other portions of the vessel, heating and vitiating the air in the hold, stores and magazines, which latter especially should be kept as cool as possible, as with some of the powders now in use (the S.B.C. and E.X.E.) it is most important not to drive off the moisture which they contain, as it entirely alters their nature.

The objection which exists to making any openings in the steel deck which can possibly be avoided renders any definite system of ventilation of war ships very difficult, but it is absolutely essential that some more efficient system than that at present adopted, should be employed in the newer types of war ship.

The bellmouth canvas cowls when properly set and when the ship is going at full speed act in driving air into the ventilation trunks between deck, but when the ship is at rest unless a high wind is blowing they are perfectly inactive and in bad weather have to be closed in order to prevent water finding its way down, besides which even when they are acting no provision is made for removing the vitiated air. A far more effective method of meeting the difficulty would be the adoption in the Navy of some such method of ventilation as that which took the prize given by the Shipwrights' Company, in 1882, for the best system of ventilation for steam ships. In this scheme, cowls are replaced by water tight down draughts, which supply an abundant quantity of air to all parts of the vessel, whilst self acting air pump ventilators extract the vitiated and heated air from every part of the ship.

CHAPTER XIV.

EXPLOSIVES—GUNPOWDER.

Nature and causes of explosion—Exothermic and endothermic compounds — Classification of explosives — Gunpowder — Ingredients and composition—Saltpetre—Occurrence in Nature—Artificial preparation—Purification—Chemical decompositions of saltpetre—Charcoal for gunpowder — Sulphur — Occurrence in Nature, preparation, purification and properties — Manufacture of gunpowder—Mixing, milling, breaking down, pressing, granulating, dusting, glazing, stoving, finishing and blending—Pebble and prism powder—S.B.C. and E.X.E. powder—Built up charges—Requirements of a good cannon powder—Effect of the prismatic form on the rate of burning of powder—Measurement of the pressure during firing powder — Crusher gauge — Muzzle velocity — Boulengé chronograph—Effect of moisture and density on pressure and muzzle velocity—Chemical changes taking place during the combustion of gunpowder—Gaseous and solid products formed—Method of calculating volume of gases produced and pressure exerted — Gases from S.B.C. and E.X.E. powders—Amide powders.

IT can readily be proved that when organic substances containing hydrogen undergo decay, some of the hydrogen present unites with the oxygen of the air to form water, and the heat generated by the combination is spread over so long a period, that at no one moment of time is it perceptible to the senses. If, however, hydrogen gas is confined under pressure in a gas holder, and allowed to escape through a jet into the air, on being ignited it burns with an intensely hot flame, the heat energy of which can be converted by suitable contrivances into other forms of energy, such as mechanical force. In this case, as much hydrogen is converted into water in the course of a minute, as would have been formed in some years by the process of slow combustion, and the increase in calorific intensity obtained is solely due to the increased rate of combustion, the total thermal value of the hydrogen being the same, whether it is burnt by a slow process taking years, or rapidly in a minute. If now the same volume of hydrogen be mixed with sufficient air to supply it with the oxygen required to convert it into water, and if a light be applied to the mixture, the molecules of hydrogen being side by side with the oxygen necessary for their conversion into water, combustion takes place with enormous rapidity, and the intense heat generated expands the vapour formed to such an extent, that an explosion results.

It is, therefore, evident that explosion may be looked upon as being intensely rapid combustion. Rapidity of combustion by increasing the calorific intensity expands the products of combustion, if they be gaseous, to an enormous extent at the moment of their formation, and as the effect of explosion is dependent upon the sudden generation of a large volume of gas from as small a volume as possible of original matter, the amount of heat generated during explosion is an important factor in the value of an explosive.

In an effective explosive these two essentials must be combined, and a solid or liquid occupying a small bulk must contain within itself the constituents necessary for building up a large volume of gas, whilst the change in condition must take place infinitely rapidly and generate so much heat that the volume of the gaseous products is again largely increased by expansion.

The smaller the space into which the original explosive can be packed the greater will be the effect produced; a mixture of air and hydrogen explodes, but the explosion is much more violent if the same quantity of hydrogen is mixed with pure oxygen instead of air, as the retarding influence of the nitrogen is removed and the mixture occupies less than one half of the space occupied by the air and hydrogen.

The explosion of a mixture of hydrogen and oxygen produces a pressure of 240 pounds on the square inch, which is very small as compared with gunpowder, which gives on explosion a pressure of 30 tons on the square inch, this being due to the fact that the ingredients of the powder are solid and therefore occupy the minimum amount of space; if the mixture of hydrogen and oxygen were compressed to the same density as gunpowder, it would develop on firing a pressure of over 300 tons on the square inch.

Oxygen in the gaseous form could not be used in explosives as it would occupy too large a space, but there are certain compounds rich in oxygen, which hold it in such feeble combination and are so ready to give it up to bodies capable of being oxidised, that they can be used as a form of compressed oxygen and by their decomposition they supply to the combustibles present in the explosive the oxygen necessary to convert them into large volumes of gases.

In nearly all cases of chemical decomposition heat is absorbed, and the compounds which behave so are called "exothermic," because in their formation heat was given out, but the oxidising compounds used in most of the explosives are exceptions to this law, and during decomposition evolve heat which helps the action, these compounds being called "endothermic."

It is of great importance that the combustible and the supporter of combustion in an explosive mixture should be in as fine a state of division as possible and well mixed, so that at the moment of explosion, each molecule of combustible shall find itself side by side with the molecules with which it is to combine, and that as little inactive material as possible should be present. The important effect of these conditions may be shown by taking four small pieces of phosphorus of equal size, and placing one on a saucer, when it will enter into slow combustion with the oxygen of the air, and if the day be warm, the temperature may rise to the point necessary for rapid combustion; but if not, many hours will have elapsed before the action is complete and the last of the phosphorus oxidised. The second piece can now be ignited in a deflagrating spoon and immersed in a bell jar of air, when it will burn away in a few minutes with evolution of heat and light; whilst if the third piece be now in the same way ignited and plunged into a jar of pure oxygen, it will burn away still more rapidly and the increase in calorific intensity is shown by the bright light produced.

If now the fourth piece of phosphorus be dissolved in a few drops of bisulphide of carbon, and this solution be poured upon a small heap of powdered potassic chlorate, placed on a piece of blotting paper supported on the ring of a retort stand, the bisulphide will evaporate and will leave the phosphorus in a very finely divided condition on the surface of the chlorate, a violent explosion at once ensuing, caused by the spontaneous ignition of some of the finely divided phosphorus which causes the chlorate to decompose and give up its oxygen. This is an "endothermic" decomposition and the heat so generated together with the heat produced by the combination of the phosphorus and oxygen, gives, on account of the rapidity of the action, great calorific intensity, causes enormous expansion and consequent violence of explosion.

The intense rapidity of combustion was in this case due to the fineness of division of the phosphorus, and to the small bulk into which the oxygen was compressed, the chlorate necessary to burn the phosphorus only occupying roughly $\frac{1}{600}$th the volume of oxygen necessary, or $\frac{1}{3000}$th the volume of air.

The explosives in use may be classified into mixtures and compounds: the former class containing the combustible, and the oxygen supplying substance in the condition of intimate mechanical mixture, whilst the latter class consists of organic compounds, containing oxygen loosely held in combination by nitrogen, and which oxygen on any disturbance of the molecular structure of the compound enters into new combinations with the carbon and hydrogen already present in the molecule. In some of the new explosives these two classes are combined, and the gas generating power of the second class is augmented by the admixture of highly oxidising substances which tend to render the combustion more complete and so increase the amount of heat generated.

Gunpowder, which is the most important and the most commonly used of the explosives, is an example of the first class, being an intimate mixture of potassic nitrate or saltpetre, sulphur and carbon.

The use of gunpowder for purposes of war dates in the English Service from 1346, when it was used by the English army at the battle of Crecy, but methods for its preparation and use seem to have been known to the Chinese long before the Christian era. English Service powder has the average composition :—

Potassic nitrate	75
Charcoal	15
Sulphur	10
	100

Although in some of the new slow burning prismatic powders the percentage of potassic nitrate and charcoal have been increased and less sulphur used, the Service powders of various foreign governments approximate closely to this composition :—

COUNTRY.		Potassic nitrate.	Charcoal.	Sulphur.
England	Black powders	75	15	10
	Brown cocoa	79	18	3
Sweden		75	15	10
Russia		75	15	10
Prussia		74	16	10
Saxony		74	16	10
United States		76	14	10
Austria		75·5	14·5	10
France		75	12.5	12.5
Belgium		75	12.5	12.5
Germany		76	14	10

The value of a powder is, to a great extent, dependent upon the purity of its constituents, and the processes by which it is mixed, as well as on the form in which it is finally made up, and in the manufacture of Service powder all these points must receive the greatest attention.

Potassic nitrate, nitre or saltpetre (KNO_3) is the ingredient in powder which supplies the oxygen necessary for the combustion of the carbon. Its name "saltpetre" means salt of rock, from the fact that it is found in small crystals upon the surface of certain rocks containing potassium, which has combined with nitric acid present in minute traces in the air.

The salt can be formed by neutralising nitric acid with a solution of potassic hydrate, when :—

$$\overset{\text{Nitric acid}}{KNO_3} + \overset{\text{Potassic hydrate}}{KHO} = \overset{\text{Potassic nitrate}}{KNO_3} + \overset{\text{Water.}}{H_2O},$$

and from this solution the salt can be crystallised in six sided prisms. When pure it contains :—

Potassium	38.7
Nitrogen	13.8
Oxygen	47.5
	100.0

Saltpetre occurs in Nature as a deposit in certain parts of India, and large quantities are obtained from Bengal and Oude, where it is extracted from the earth by treating it with water, and after filtering, allowing the solution to evaporate in shallow pans, the crystals so obtained being exported under the name of "grough" saltpetre, which however is far from pure, the usual composition being about—

Potassium nitrate	93.95
Sodium sulphate	3.21
Sodium chloride	.85
Sand	.25
Water	1.74

If this saltpetre be heated to 335° C. it melts, and can be cast into cakes, which on breaking exhibit a crystalline fracture, which varies in appearance with the amount of impurities present, a property which at one time was used to roughly indicate the value of any sample of the salt, and was called the "refraction" of the nitre. The term is to a certain extent still retained to indicate the amount of impurities present, and the sample of nitre, of which an analysis is given above, would be quoted as having "6 per cent. refraction."

This "grough" saltpetre has be to very carefully purified for use in the manufacture of gunpowder, which is done by recrystallising it. 100 grams of water will at 100° C. dissolve 200 grams of saltpetre, whilst at 21° C. it will only dissolve 30 grams; if therefore a saturated solution of saltpetre is made in boiling water and is then allowed to cool down, $\frac{17}{20}$ths of the dissolved salt will crystallise out, and the impurities present being not much more soluble in hot water than in cold, they will remain in solution.

In practice this is done in refining coppers capable of holding about 500 gallons each, and fitted with false bottoms of perforated iron to allow sand and other insoluble impurities to sink through. These vessels are charged with about 280 gallons of water which has been used in a latter operation for washing the crystals of saltpetre, and which, therefore, contains already some of the salt in solution, and into this liquor about 40 cwt. of crude saltpetre is put. After heating the coppers for about two hours, the whole of the saltpetre is dissolved and the boiling point of the liquid raised by its presence to nearly 110° C., and the specific gravity to 1.49; during the boiling a scum forms on the top of the liquid and from time to time a little fresh water is added to facilitate the separation and rising to the surface of the impurities which form the scum. When scum ceases to rise, the coppers are filled up with cold water, the solution raised to the boiling point again and the fires drawn; in about two hours the liquid has cooled down to about 105° C., and at this temperature it is pumped out into troughs, from which it filters through bags of "dowlas" into a second trough leading to the copper crystallising tanks.

These tanks are about 12 feet by 7, and not more than a foot in depth; about 6 inches of liquid is run into each tank, and having now cooled down to about 85° C., crystallisation commences. If the liquor were allowed to remain at rest in the tanks, large crystals would form, and it is important to avoid this, as some of the "mother liquor" (so called because it has given birth to the crystals) would be enclosed in cavities and cracks and would render the crystals impure, and to prevent this a workman keeps the liquid in a state of agitation by means of wooden hoes: very small, finely divided crystals rapidly separate and by means of perforated copper shovels are removed and placed on sloping draining boards at the side of the tanks to allow the liquor to drain from them, and are then passed on to the washing vat.

After the temperature in the crystallising tank has fallen below 32° C., the stirring is discontinued and no more crystals are withdrawn, as they only separate slowly and might contain traces of impurities; all the saltpetre now remaining in solution being worked up again with fresh batches of the grough saltpetre.

The fine crystals called "saltpetre flour" are placed in the washing vats, the size of which is roughly 6 feet by 4 and 3 feet 6 inches deep, and they are fitted with false bottoms perforated with holes, whilst below the false bottom and in front of the vat is a plug-hole, which can be opened or closed at pleasure, The vat having been filled with "flour" the plug is taken out and the crystals are washed with about 70 gallons of water and then allowed to drain. The plug is again replaced and the crystals are covered with water and allowed to soak for half an hour when this second wash water is run off and the crystals again allowed to drain, after which a third and final washing is given with about 100 gallons of water. These wash waters are all collected in a tank and are used for dissolving the grough saltpetre in the "refining coppers."

The washed saltpetre flour is now allowed to drain for 12 hours, and the upper portions are then sufficiently dry to remove to the store bins, where it remains until required. The percentage of moisture varies from 3 to 5 per cent., and is accurately determined and allowed for before the saltpetre is worked up into powder. In the Government Powder Mills at Waltham Abbey, nothing is used but Indian saltpetre, purified as described, but most of the small grain powder is now manufactured by private firms, and a considerable portion of the saltpetre is obtained from sodic nitrate, found in Chili and Peru in large deposits and called "Chili saltpetre." Sodic nitrate itself could not be used instead of saltpetre as an ingredient of gunpowder in climates containing much water vapour in the air, as it is hygroscopic—that is, it has the power of attracting and absorbing moisture, which would cause the disintegration of the powder, but in hot, dry climates it is often used for making rough and blasting powders. Sodic nitrate can, however, be easily converted into potassic nitrate by double decomposition with boiling concentrated solution of potassic chloride, which forms potassic nitrate and sodic chloride, these two salts being separated by crystallisation :—

$$\overset{\text{Sodic nitrate}}{NaNO_3} + \overset{\text{Potassic chloride}}{KCl} = \overset{\text{Potassic nitrate}}{KNO_3} + \overset{\text{Sodic chloride.}}{NaCl.}$$

This reaction being due to the fact that sodic chloride is far less soluble in hot water than potassic nitrate.

	100 parts of	
	Boiling water dissolve	Cold water dissolve
Sodic nitrate	218 ...	50
Potassic nitrate	200 ...	30
Sodic chloride	37 ...	36
Potassic chloride	53 ...	33

So that when a hot concentrated solution of sodic nitrate is taken and potassic chloride added to it little by little, sodic chloride forms and crystallises out, being removed from the solution by perforated ladles, whilst the mixture of salts remaining behind is roughly separated by crystallising, and then purifying in the same way as the "grough saltpetre." The potassic chloride used in this process is obtained from great mines at Stassfurth, in Saxony, and also from the vegetable refuse left after the manufacture of sugar from beetroot.

The deposits of saltpetre in India and elsewhere are due to the decomposition of animal refuse containing carbon, hydrogen, nitrogen and oxygen, which, during processes of decay become chiefly converted into ammonia and carbon dioxide, and the ammonia by a process of oxidation in the porous soil, aided by a certain form of "mycoderm" becomes converted into nitric acid which combines with the potassium which is to be found in all fertile soils and forms saltpetre.

When the urine of human beings and animals is undergoing putrefactive decay, the urea and water which it contains give rise to ammonic carbonate, the smell of which is very distinct in stables and urinals.

$$\begin{array}{ccccc} \text{Urea} & & \text{Water} & & \text{Ammonic carbonate.} \\ N_2H_4CO & + & 2(H_2O) & = & (NH_4)_2CO_3. \end{array}$$

If the putrefying urine be covered with porous soil, the smell of ammonia disappears, the gas being absorbed by the soil and in the presence of an organised ferment abundant in soil and sewage, undergoes a process called "nitrification" which is aided by weak alkaline bodies, and which consists of the conversion of the ammonia by oxygen absorbed from the air, into nitric acid, which then combines with more ammonia to form ammonic nitrate—

$$\begin{array}{ccccccc} \text{Ammonia} & & \text{Oxygen} & & \text{Nitric acid} & & \text{Water.} \\ NH_3 & + & 2O_2 & = & HNO_3 & + & H_2O, \end{array}$$

and

$$\begin{array}{ccccc} \text{Nitric acid} & & \text{Ammonia} & & \text{Ammonic nitrate.} \\ HNO_3 & + & NH_3 & = & NH_4NO_3, \end{array}$$

whilst the ammonic nitrate in contact with salts of potassium in turn is decomposed, and potassic nitrate results.

This process has been used during dearth of saltpetre in time of war and answers very well for its artificial production, sewage being made into a heap with loamy soil and the ashes of various plants rich in potassium salts. The late Professor Bloxam calculated that the urine of a man would furnish 2 oz. of saltpetre a day, an amount sufficient to make nine rounds of small arm ammunition.

The refined saltpetre has now to be tested to see that it is pure, and it should be neutral to red and blue litmus paper showing the absence of any free acid or alkali; it should give no cloudy or milky appearance when a solution of nitrate of silver is added to some of it dissolved in distilled water, showing the absence of any trace of chlorides; and, finally, a solution of it must give no precipitate with baric chloride, which would indicate that some sodic sulphate was present.

It is especially important that no trace of chloride should be left in the saltpetre as both sodic and potassic chlorides have the power of attracting and absorbing moisture from the air, which would tend to reduce the power and rapidity of explosion of the powder, and would also cause the grains to crumble.

Saltpetre crystallises in long grooved six sided prisms; when heated it fuses at 335° C., and on continuing the application of heat it commences to decompose. At a red heat this decomposition consists of the evolution of one third the oxygen contained in the salt and the formation of potassic nitrite.

$$\underset{\text{Potassic nitrate}}{2(KNO_3)} = \underset{\text{Potassic nitrite}}{2(KNO_2)} + \underset{\text{Oxygen.}}{O_2}.$$

Whilst at a still higher temperature, the nitrite undergoes decomposition with evolution of nitrogen as well as oxygen, and formation of potassic oxide and peroxide.

$$\overset{\substack{\text{Potassic}\\\text{nitrite}}}{6(KNO_2)} = \overset{\substack{\text{Potassic}\\\text{oxide}}}{2(K_2O)} + \overset{\substack{\text{Potassic}\\\text{peroxide}}}{K_2O_2} + \overset{\text{Nitrogen}}{3N_2} + \overset{\text{Oxygen.}}{4O_2}.$$

When dried and finely powdered saltpetre is thrown upon red hot charcoal, the carbon undergoes rapid combustion at the expense of the oxygen of the nitrate, and in the same way when powdered carbon is thrown upon fused potassic nitrate violent combustion takes place, the reaction probably being:

$$\overset{\substack{\text{Potassic}\\\text{nitrate}}}{4(KNO_3)} + \overset{\text{Carbon}}{C_5} = \overset{\substack{\text{Potassic}\\\text{carbonate}}}{2(K_2CO_3)} + \overset{\substack{\text{Carbon}\\\text{dioxide}}}{3(CO_2)} + \overset{\text{Nitrogen.}}{2N_2}.$$

One part (by volume) of solid potassic nitrate contains as much oxygen as 3,000 times its own bulk of air, and it is this fact which renders it so valuable in gunpowder, in which it may be looked upon as being a store of condensed oxygen to be used for the combustion of the carbon.

The carbon used in gunpowder consists of charcoal prepared with great care from various vegetable tissues, the nature of which depends upon the character of the powder in which it is to be used. Great care has to be taken in regulating the temperature at which the substances are carbonised, as if a high temperature is employed a very dense charcoal is obtained, which as it is not easily combustible, is not so good for use in powder as a charcoal made at a lower temperature. The reason of this is that woody fibre consists mainly of cellulose ($C_6H_{10}O_5$), and the higher the temperature employed the greater the percentage of oxygen and hydrogen eliminated, and with the elimination of the hydrogen the inflammability is decreased.

The difference in composition of the charcoal formed at various temperatures is strikingly shown by the following table:—

PERCENTAGE COMPOSITION OF CHARCOAL.

Temperature.	Carbon.	Hydrogen.	Oxygen.	Ash.
270° C.	71.0	4.60	23.00	1.40
363°	80.1	3.71	14.55	1.64
476°	85.8	3.13	9.47	1.60
519°	86.2	3.11	9.11	1.58

In the Government Powder Factory the following woods are used :—

Powder.	Wood.	Time of burning (hours).
M.G.$_1$., R.F. G....	Dogwood	4
R.F.G.$_2$		8
R.L.G.$_2$	Alder and willow.	3½
R.L.G.$_4$, P. ...		4
P$_2$		6
Prism (black) ...		4
S.B.C. (slow burning cocoa prism)	Straw.	

The temperature of carbonisation varying between 360° C. and 520° C., whilst the rapidity with which the maximum temperature is reached also has an important influence on the quality of the charcoal formed, the quicker the heating the higher being the percentage of carbon formed.

Charcoal which has been carbonised at temperatures below 260° C. has a brown colour and is highly inflammable, and although the large percentage of oxygen left in it reduces its calorific value (see under fuel, p. 175), yet where it is important to retain a certain portion of moisture in the powder, as is the case with the new E.X.E. and S.B.C. prism powders, in which a given quantity of moisture is almost as important an ingredient as the sulphur, then the hygroscopic properties of the lightly burnt charcoal are of great value in the closely pressed prisms. Some of the brown charcoals are carbonised in retorts heated by superheated steam instead of directly by fire.

In the manufacture of gunpowder, the charcoal is prepared by taking sound young alder and willow wood grown in this country, or alder buckthorn, commonly called, "black dogwood," and which is mostly imported, stripping off all bark and thoroughly air drying it by exposure in sheds or thatched stacks, until the percentage of water is reduced to not more than 20 per cent., which takes place after a year or eighteen months' exposure.

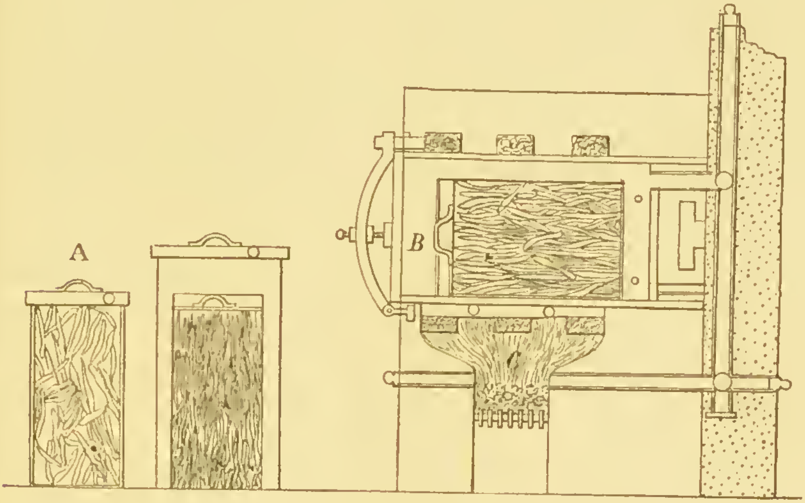


Fig. 41.

The wood is then cut into strips three feet long and packed into round iron vessels called "slips" (A, Fig. 41), which are three feet six inches long, and two feet four inches in diameter, the bottom being perforated with two holes. A lid is fitted on to the slip and it is then placed in horizontal iron cylinders, called retorts (B), which are closed by gas tight doors and have openings at the end communicating by pipes with the furnace below (C), which latter is so constructed that the heat can be regulated with great nicety. During the charring of the wood, the gases and vapours escaping from the retort are led down into the furnace, burning there and saving a certain proportion of fuel, and also giving a luminous flame, which, being replaced by a pale blue flame of carbon monoxide, marks the end of the process.

Sulphur is one of the few elements found uncombined in Nature, large quantities occurring as deposits in most volcanic districts, and it was from beds of this native sulphur found in Sicily, that for many years the sulphur was obtained for the sulphuric acid and gunpowder factories in this country; but the imposition of a heavy tax upon the export, caused manufacturers to seek other sources of supply, and at the present time most of the sulphur used in this country is obtained from iron pyrites, a double sulphide of iron and copper which is obtained in considerable quantities in various parts of the world, and from which sulphur can be obtained by a process of distillation. The sulphides of the metals are as a rule their most common ores, and besides the enormous amount of sulphur combined as sulphide, it is also extensively distributed in combination with metals and oxygen as "sulphates," such as gypsum (calcic sulphate), heavy spar (baric sulphate), Epsom salts (magnesic sulphate), &c.

Sulphur is remarkable for the number of different forms in which it can exist and the changes which it undergoes when heated.

At very low temperatures sulphur is nearly white, but at ordinary temperatures it has a straw yellow colour; when heated to 115° C. it melts to an amber coloured liquid, which is as fluid as water, and on allowing this to cool until a crust forms on the outside of the mass, if holes are broken in this crust and the still fluid portion is poured out from the interior and the mass broken open, it is found to have crystallised in needle shaped oblique prisms which are perfectly transparent when freshly made, but which soon become opaque on keeping, due to the mass having become converted into minute rhombic octahedra, a change attended with evolution of heat.

On heating sulphur above 115° C., it gradually darkens in colour and becomes more and more viscid, until at 180° C. it is nearly black and so thick that the vessel in which it has been melted can be turned upside down without any running out. Some change in condition of the sulphur evidently occurs about this point, as if a thermometer is immersed in the sulphur it remains stationary although heat is being poured into the sulphur, showing that heat is being rendered latent; after a short time, however, the temperature again begins to rise, the viscid sulphur becoming again more and more liquid, until at 250° C. it can again be freely poured out, although it is not so liquid as at 115° C. If sulphur liquefied at 260° C. is poured in a thin stream into a large vessel of water it forms an elastic semi-transparent mass, very much resembling india-rubber; but this plastic form is not permanent, and on keeping gradually becomes yellow and brittle, being reconverted to the crystalline condition, and if the mass be broken up and examined under a magnifying glass the particles will be seen to be octahedral in form.

This change from the plastic to the crystalline form is attended with evolution of the heat rendered latent at 180° C., and the two forms of sulphur exhibit such wide differences in their behaviour that they are looked upon as allotropic modifications of the element. Plastic sulphur is insoluble in bisulphide of carbon, but both the crystalline varieties readily dissolve, and if the solvent is allowed to spontaneously evaporate, the sulphur is left in octahedral crystals of the same form as that in which it is found native. The crystalline sulphur soluble in bisulphide of carbon has been shown to be electro negative, whilst the insoluble forms of sulphur are electro positive. On continuing to heat sulphur above 260°

no further change takes place until 444° C. is reached, when it boils and is converted into vapour.

Three chief forms of sulphur are described—the octahedral, the prismatic, and the plastic or "amorphous" (*i.e.*, without crystalline form), while the fact that it forms two distinct kinds of crystals causes it to be classed with those substances which are called "dimorphous" (having two crystalline forms). Sulphur has an atomic weight of 32. The existence of various forms of sulphur may to a certain extent be explained by the presence of a varying number of atoms in the molecule, and this idea is supported by the density of sulphur vapour, which at 500° C. is 96, but steadily diminishes with increase of temperature above 700° C. and becomes constant at 1,000° C. when it is 32. At 500° C. therefore the molecule of sulphur must contain 6 atoms instead of 2, and it is quite possible that at lower temperatures a further increase in the number of atoms in the molecules may take place.

Sulphur in its combining powers very much resembles oxygen and will enter directly into combination with all the non-metals, with the exception of nitrogen, and with most of the metals.

To obtain sulphur from the mixture of marl, limestone or gypsum with which it is found native, a heap is generally made and some of the sulphur kindled, which by its combustion melts the remainder, and on choking out the fire the melted sulphur runs from the bottom of the heap; or the crude mixture may be heated in iron vessels by superheated steam which melts the sulphur and causes it to flow away from the impurities with which it was mixed, and it is then run into wooden moulds.

When iron pyrites is heated out of contact with air, it gives off half its sulphur, a reaction which may be represented by—

$$\underset{\text{Iron pyrites}}{FeS_2} = \underset{\text{Ferrous sulphide}}{FeS} + \underset{\text{Sulphur.}}{S.}$$

As imported into this country sulphur contains 3 or 4 per cent. of sand, clay and other impurities, and before it can be used for powder making, it must undergo a process of refining. The sulphur used at Waltham Abbey is still imported from Sicily, and is known in the trade as "Licara firsts" and about 7 cwt. of this is placed in the melting pot (A, Fig 42), the tube to the condensing dome (C) being left open, whilst that leading to the receiving pot (B) is shut; after heating for about two hours, the vapour of sulphur begins to distil over into the dome, and condenses on the sides and floor as the fine powder known as "flowers of sulphur." After heating for about three hours, the colour of the sulphur vapour becomes very dark, and the tube leading to the dome is then shut and the tube to the receiver (B) opened: this tube (D) is cooled by a current of cold water which is kept flowing through a jacket which surrounds it, and the vapour of sulphur condenses to an orange liquid, and flows into the receiving pot, where it is allowed to cool to a temperature of about 120° C., and is then ladled out into moulds. The solid impurities are left behind in the retort and are cleaned out occasionally.

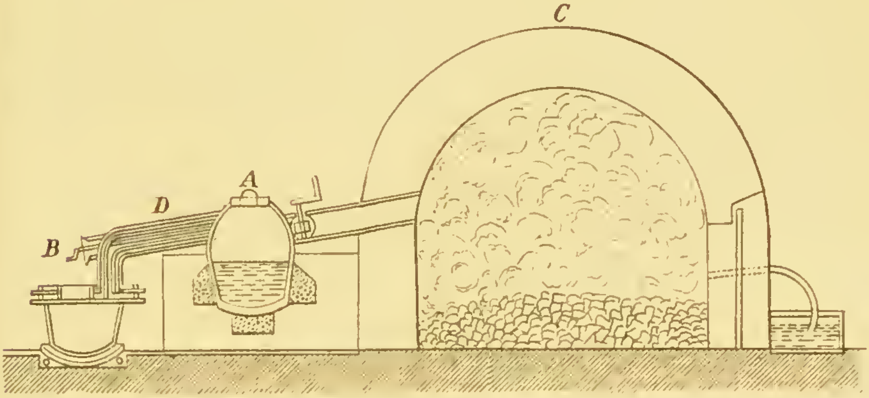


Fig. 42.

The "flowers of sulphur" which condensed in the chamber is never used for powder making, as it contains small quantities of sulphur acids which render it unfit for this purpose, and it is returned to the retort with a fresh quantity of the "grough" sulphur for redistillation.

The distilled sulphur is when cold removed from the moulds, and having been broken up, is then ground under a pair of iron edge runners, about 2 cwt. being crushed at a time; it is then sifted through 36 mesh wire cloth sieves, and the portion which passes through is ready for use, whilst the coarser pieces are returned to the mill.

Sulphur to be used for powder making should not leave more than 0.25 per cent. of residue when burnt, and when boiled with water should not render it perceptibly acid, although a very faint reddening of litmus is not considered sufficient ground for rejecting a sample.

Sulphur in gunpowder has several important functions to perform: in the first place it lowers the point of ignition by itself inflaming at a temperature of 260° C., and by its combustion quickly raising the temperature to the fusing point of the saltpetre, 335° C., which, but for the presence of the sulphur, would determine the point of ignition of the powder. As soon as the fusing point of the saltpetre is reached, it oxidises the remaining sulphur and, in so doing, gives out much more heat than is evolved by the oxidation of the carbon, accelerating the combustion, and also expanding the gases produced; so that at the moment of explosion they occupy a larger volume than would be the case if no sulphur were present.

The effect which sulphur has in increasing the rate of combustion may be shown by making two trains of equal length, one of ordinary small grain powder, and the other of the same powder from which sulphur has been abstracted by treating it with bisulphide of carbon, and if these be simultaneously fired it will be found that that containing sulphur will have burnt through its entire length, whilst that without sulphur will not have burnt through more than half its length in the same time.

The saltpetre is not ground before use, but the charcoal is ground in an enclosed mill until it will pass through a 32 mesh sieve, and the ingredients are then ready for the manufacture of the powder: the first three processes entailed are the same for all kinds of powder; they are:—

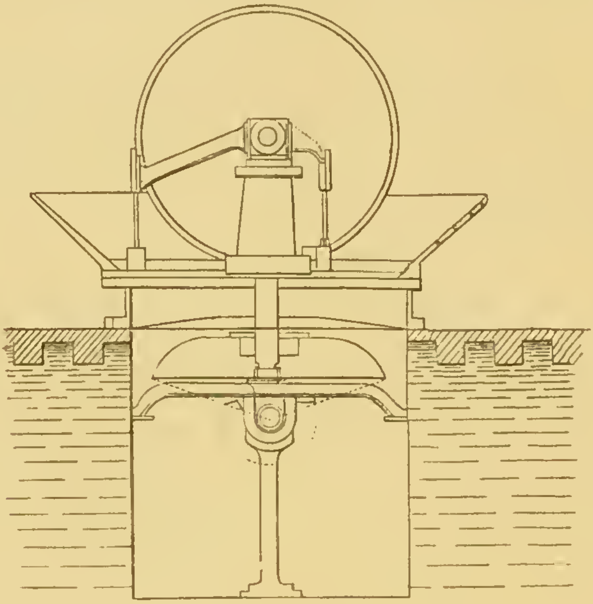
1. Mixing the ingredients.
2. Incorporating or milling them.
3. Breaking up the mill cake.

The ingredients of the powder are first accurately weighed out, allowance being made for the moisture present in the refined saltpetre, and are then mixed in charges of from 50 to 60 pounds in a revolving gun metal drum, which contains arms revolving in an opposite direction to the drum itself; the mixture is then passed through a coarse copper sieve to make sure that no foreign solid material is present and is then called "green charge." This is now taken to the incorporating mill, which consists of two iron or stone edge runners, weighing from three to four tons, which revolve on a bed made of the same material as the runners themselves, and having a sloping rim (Fig. 43). The runners are worked by machinery from below and make seven to eight revolutions per minute.

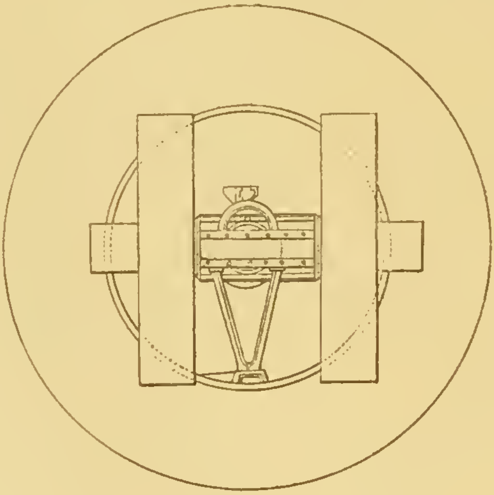
The green charge is placed on the bed of the mill and is moistened with a very small quantity of distilled water, to prevent any of the charge flying about as dust and also to aid the incorporation.

The green charge is milled for from three to eight hours, according to the nature of the powder, and a workman constantly pushes the charge from the outside to the middle of the bed plate with a wooden "shover," so as to keep it under the runners.

The incorporating mills are in a long building containing six mills, each of which is shut off from the next by a partition, whilst over each mill is an iron cistern connected by a lever arm to a large wooden shutter which is exactly over the bed of the mill, explosion of the charge would raise the shutter and deluge the mill by upsetting the tank; all the tanks work



(A)—Fig. 43.



(B)—Fig. 43.

on one shaft, so that the upsetting of one would drown the charges in all the mills.

The "mill cake" as the charge is now called is perfectly uniform in appearance and should contain from 1 to 3 per cent. of moisture if it is to be used for small grain powders, and 3 to 6 for the larger kinds. It is next conveyed to the breaking down machine, where the mill cake is placed in a hopper, and is carried by an endless band to the top of the machine and then falls between a pair of grooved rollers, and afterwards between plain rollers which break it into what is termed "meal." In making all the small arm and R.L.G. powders, this meal is now packed in layers in the press box and subjected to a pressure of about 70 tons on the square foot for about a quarter of an hour, which renders it excessively hard and compact, and as far as its composition goes, it is now gunpowder, but in order to regulate its rate of combustion it must be granulated to the required size, which is done in a machine much resembling the breaking down machine. Here the "press cake" has to pass through successive pairs of grooved gun metal rollers, which break it up into grains and from which it falls into sieves which are continually vibrating and being fixed at an angle below the rollers, sort the grains into the various sizes required, and shoot them out into boxes placed to receive them.

Powders made with "dogwood" charcoal are very dusty, and when they leave the granulating machine, are passed through an inclined wooden framed cylinder covered with 20 mesh copper gauze and making about 40 revolutions per minute, the dust passing through the gauze and the grains passing out at the lower end. The powder now goes to the glazing drums in which it is placed in charges of about 900 lb. at a time, and the drums are driven at about 12 revolutions per minute, for from 1½ to 10 hours according to the kind of powder; this imparts by mere friction a fine glaze to the surface of the smaller grained powders, but with the larger powders it is necessary to add a small quantity of graphite.

The glazed powder is now put in a drying room heated by steam pipes, and through which a constant stream of air is passing to remove excess of moisture, and then is "finished" by a second glazing in a horizontal "reel," which rotates at high speed. The finished powders are then blended, *i.e.*, several batches are mixed together so as to give as uniform a quality of powder as possible, and are ready for use.

In making pebble powders the press cake is made of particular thicknesses, $\frac{5}{8}$ and $1\frac{1}{2}$ inch respectively, and the press cake is then cut into cubes of the required size, which are glazed, stoved, finished and blended as before.

Prismatic powder, which has now to a great extent superseded pebble powder for the larger guns, is made by taking the granulated press cake and compressing it in an hydraulic press machine (Fig. 44) into the form of regular six sided prisms. These prisms are made under enormous hydraulic pressure in phosphor bronze moulds, and are perforated by a hole through the centre, so that when built up in the cartridge the flame can have free access from end to end of the whole charge.

Great attention is paid to the stoving of the new forms of prism powder (E.X.E. and S.B.C.), as the amount of moisture in these has an important bearing upon their rate of explosion, and they are dried first for 24 hours at 32° C., and then for 12 hours at 60° C., which leaves them with from 1.7 to 2.2 per cent. of moisture, which is the normal amount which these powders retain under ordinary atmospheric conditions.

The old form of prism powder (black) had the same composition as the pebble and R.L.G. powder, but in both the new types of prism, the S.B.C. and E.X.E. powders, the amount of sulphur is considerably decreased, whilst very lightly charred carbon is used to make up for this and to give a powder fairly easy of ignition; it is customary, however, in making up the cartridges of the new brown powders to put in the base two or three black prisms, to take the flash and ensure ignition of the remainder of the charge. The E.X.E. is intended to replace black prism and P_2 powder in the 6 inch breechloading and R.M.L. guns. This prism powder is distinguished from the other prisms by its slate colour, and by a groove moulded in it and surrounding the central core (Fig. 45). The S.B.C. prism powder is recognisable by its brown colour and by the circular indentation round the core (Fig. 45). The S.B.C. powder is for use in the 13.5 inch (68 ton) and 16.25 inch (110 ton) guns.

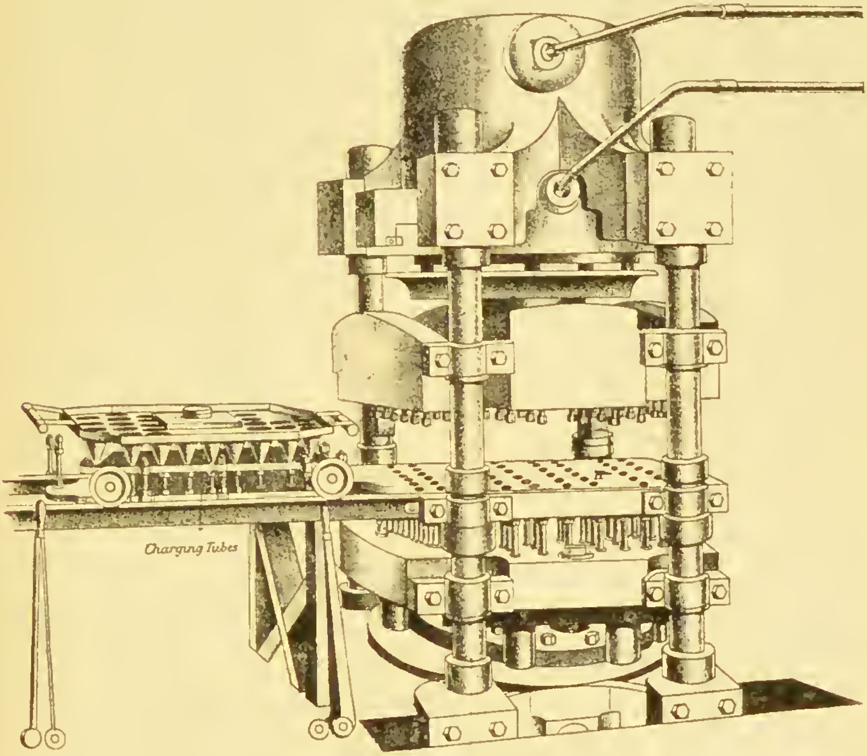
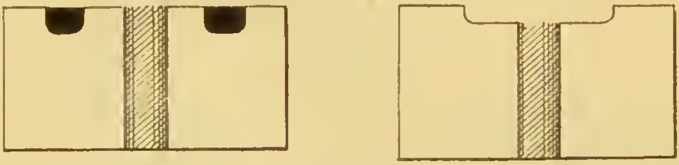


Fig. 44.

These new forms of prism powder have effected a complete revolution in gunnery and guns, as they have enabled the combustion to be so regulated that the strain upon the gun is reduced to a minimum, whilst greatly increased velocities have been obtained, and the regularity of results obtained has practically removed these powders from the ranks of "explosives" and made them true "propellants."

With the introduction of rifled ordnance 25 years ago a change came over the science of gunnery, and an enormous increase in the size of the guns, and in the charge of powder used, followed. During the Crimea the largest guns used were 68 pounder smooth bore guns weighing 112 cwt. and using a charge of 18 lb. of powder, whilst at the bombardment of Alexandria the smallest gun used was a 6½ ton one, using a charge of 30 lb. of powder; and at the present time 110 ton guns are being employed with a charge of 960 lb. of powder, and it is evident that the forms of powder used must be modified to keep pace with such radical alterations in the condition under which it is to be used.



Section of E.X.E. powder. Section S.B.C. powder.

Fig. 45.

It is required of a perfect powder that when the charge is fired in the breech of the gun, the combustion shall commence comparatively slowly, so as to gradually overcome the *vis inertia* of the projectile without throwing too great a strain on the gun, and that as the projectile passes up the bore of the gun the combustion shall increase in rapidity, so as to supply, more and more rapidly, gas to increase the momentum of the shot, which should leave the muzzle of the gun with the maximum velocity. In the old fashioned R.L.G. and P_2 powders this was never secured, and such powders could not have been used in the modern long bore guns, as the rapidity with which they burnt threw an enormous strain upon the breech and would have given the maximum velocity to the projectile before it was half way up the bore of the gun, leaving friction to reduce the velocity to a considerable extent before the muzzle was reached.

In order to avoid these defects as far as possible, built up charges were resorted to and various devices employed to slow down the initial combustion, many forms being tried, and it was General Rodman of the American Service* who first tried to overcome this difficulty by building up the charge of solid slabs perforated with holes, so as to expose the minimum surface of powder at the commencement of combustion, whilst the enlarging holes exposed a greater and greater surface of powder as the space behind the projectile increased. This idea has quite lately been revived, but large perforated cakes are always liable to break and it was found far better to build up the charge of hexagonal prisms with a central core moulded in them.

It was in accordance with this idea that the black prism powder was first made, but with alterations in the form of the guns, even this was found to burn too fast and the attempts to still further slow down the initial combustion and quicken it towards the end of the action, has resulted in the adoption of the slow burning brown powders.

I am enabled through the courtesy of Major Barker of Waltham Abbey, to give a diagram (Fig. 45) showing the pressure curves of the brown cocoa powder as compared with those given by black powders, the pressures in different parts of the gun having been carefully determined by means of the crusher gauge (Fig. 48, p. 251).

In this diagram the scale at the side represents the pressure exerted in the gun in tons per square inch, whilst the form of the curves show the variations in the pressure in the interior of the gun. The line (A) is the pressure curve for P_2 powder fired in a R.M.L. gun (D), giving a pressure of 29 tons, whilst the muzzle velocity of 1,798 feet per second can be attained.

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* Rodman: *Qualities of Cannon Powder.*—Boston, 1861.

The increase in rapidity during combustion is in the prism powder due, first, to the enlargement of the core and consequent exposure of a larger surface, and secondly, to the fact that as the walls of the prism grow thin, they break up on the lines (A′ A, Fig. 47), converting the powder during the last moments of its explosion into what is practically a brown R.L.G. powder, and thus giving enormously rapid combustion due to the exposure of a large number of fresh faces.

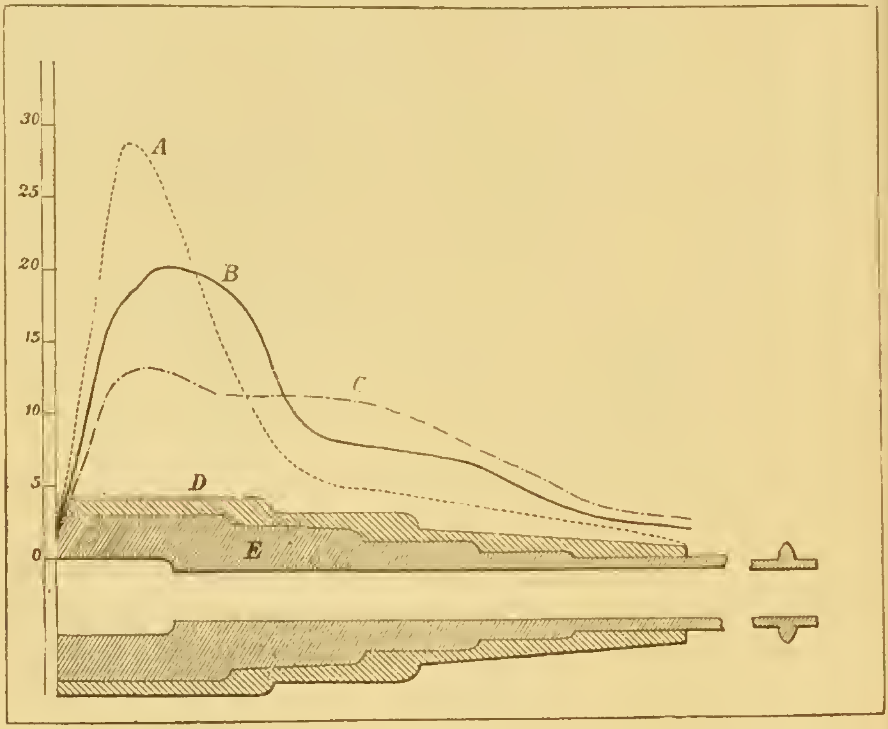

Fig. 46.

That this is really the case is shown by a prism occasionally being blown out with the projectile and extinguished by the sudden rush through the air when it is seen to have been partly consumed and broken up in the way indicated.

The pressure exerted in the breech of the gun during the explosion is measured by a contrivance called a "crusher gauge," which consists of a steel cylinder (A, Fig. 48), into which a collar (C) screws gas tight and carries a steel piston (B), also rendered air tight by the gas check (E).

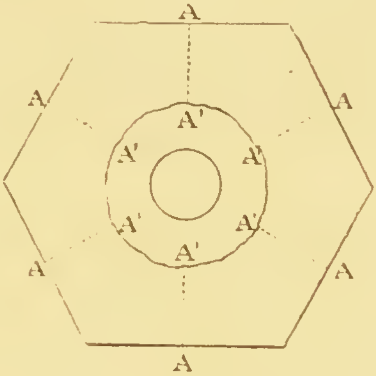

Fig. 47.

A small cylindrical piece of copper (D), which has been compressed to a known density, by exposing it to a hydraulic pressure of 12 tons, and which is 0.5 of an inch in length, is placed in the bottom of the steel cylinder; the piston is

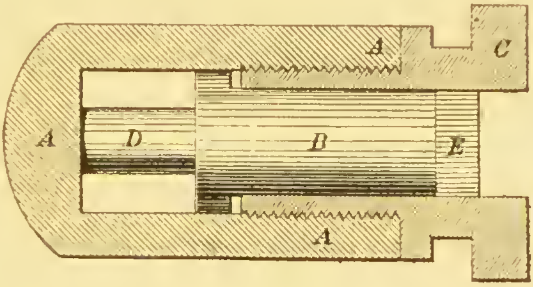

Fig. 48.

then put in its place and the collar screwed up, the gas check fitted and the crusher gauge placed in the base of the cartridge, the solid end of the cylinder being against the breech of the gun and the gas check towards the projectile. On firing the gun the gauge is subjected to the full pressure developed by the explosion of the powder, which forces the steel piston down upon the copper cylinder and compresses it. The crusher gauge having no powder behind it, is left after the explosion in the breech of the gun, and is opened and the length of the copper accurately measured on a micrometer scale, the amount of compression indicating the pressure in the breech of the gun. Used in this way the crusher gauge gives very reliable results, but it has been shown that when inserted in the wall of the gun, certain waves of pressure and difficulties in adjustment occasionally interfere with the results obtained.*

The muzzle velocity of the shot is determined by means of the chronograph. Two screens are arranged, one about 120 feet from the muzzle of the gun and the second 120 feet beyond the first. These screens consist of wooden frames strung with fine copper wire, the disruption of a single strand of which is sufficient to break the flow of a current. In the Boulengé chronograph a current from a battery of 8 Bunsen cells flows through these wires and back to the instrument house, where the wire from each frame is coiled round a separate soft iron cone and converts it into an electromagnet, each of which attracts and holds a rod of steel, the electromagnet in connection with the second frame is fixed at a lower level than the electromagnet connected with the first, and carries a short rod (A) with a weight at the bottom, whilst the first magnet is at a higher level and carries a much longer rod. The current being allowed to pass through both electromagnets, the rods are suspended in position, and by pressing the key (F) both circuits can be simultaneously broken, with the result that both the rods (A) and (B) are liberated and drop down guide tubes, the short rod (A) strikes a catch (C) and causes a knife edge to be brought against the falling rod (B) and makes a nick in it. When both rods are liberated simultaneously this nick is at the point (D). The current is again allowed to pass, and the rods hung on the electromagnets, and the gun containing the charge, the power of which is to be tested, is fired, the projectile passing through the screens 1 and 2 and breaking the current by cutting the wires. Under these conditions the long rod (B) is liberated a fraction of a second sooner than the rod (A), the result being that the nick from the knife blade is now at the point (E) instead of at (D), as in the previous case. By now measuring the distance between (E) and (D), and knowing the length of time to which this is equivalent, allowance being made for time taken in liberating knife, catch, &c., the interval of time which elapses whilst the projectile passes between screens 1 and 2 can be calculated, and being corrected for

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* Anderson. *Howard Lectures*, 1885.

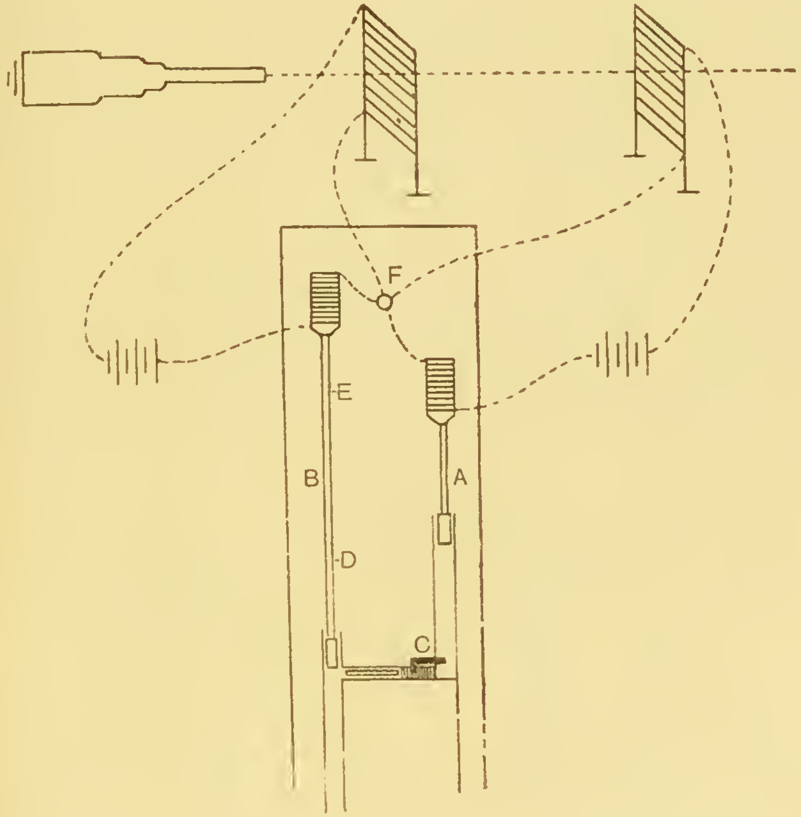

Fig. 49.

distance of screen 1 from muzzle, gives the muzzle velocity of the projectile.

Each batch of powder made is tested in this way, and the batches are then blended according to the results they have given, so as to obtain a powder best suited to the work required of it.

The best proof that can be adduced to show that the pressure gauge, when used in this way in the breech of the gun, gives reliable results is that an expert operator can, from the pressure recorded, predict within a few feet per second, what the muzzle velocity as recorded by the chronograph will be.

The uniformity of composition obtained in the Waltham processes, as described in the preceeding pages, may be inferred from the following tables of tests made on various batches of E.X.E. and S.B.C. powder, which show the very small variations in muzzle velocity and pressure given by these powders.

LOT 54. E.X.E.

Charge.	Muzzle velocity. Feet per second.	Pressure. Tons per square inch.
48 lb.	1,981	16.8
	1,978	16.6
	1,982	16.45
	1,977	16.4
	1,980	16.55
Mean	1,980	16.58

LOT 36. S.B.C.

Charge.	Muzzle velocity. Feet per second.	Pressure. Tons per square inch
360 lb.	2,020	14.75
	2,020	14.85
	2,025	14.80
	2,022	14.80

It must, however, be clearly borne in mind that this uniformity of velocity and pressure can only be obtained by absolute uniformity in density and composition of the powder, and that in order that these prism powders should yield the above results it is essential that they should contain from 1.7 to 2.2 per cent. of moisture, which shows the great importance of keeping the powder magazines of a ship as cool as possible, as the hygroscopic character of the straw charcoal burnt at a low temperature will enable the new prism powders to retain the proper amount of moisture under all normal atmospheric conditions, but when exposed to the high temperatures often observed in ill ventilated magazines situate near the boilers or engines, they must of necessity lose a certain amount of water, and abnormal pressures occasionally obtained from badly kept powder are the result.

Great attention is also paid to the density of these powders, any decrease in density tending to increase the pressure.

Density.		Velocity. Feet per second		Pressure. Tons per square inch
1.790	...	2,066	...	17.5
1.800	...	1,944	...	14.6
1.820	...	1,894	...	12.7

Ordinary fine grain gunpowder when finished should consist of hard angular grains and the mass should appear homogeneous; should not soil the hand when passed through it, and when fired on a sheet of white paper, should not scorch or burn it, and should leave but little unconsumed residue, nor should it give sparks.

The way in which powder burns is influenced to a great extent by the conditions under which it is ignited; if some powder is placed in a cylinder and touched with a hot wire, it catches fire and burns with a "puff," but if the powder is heated in a test tube at a certain temperature it explodes. In the one case the combustion spreading from grain to grain, whilst in the second case the whole mass is heated to a high temperature, and the increase of rapidity in burning is manifested by explosion. Variation in pressure has a considerable influence upon the rate at which powder will burn, as under low pressures the flame from the powder escapes so rapidly that its power of passing on the combustion from grain to grain becomes seriously impaired. If some powder is placed on a watch glass under the receiver of an air pump (Fig. 50) and is then heated by a thin platinum wire in connection with a voltaic battery, the grains of powder in contact with the wire will fuse and burn, but the remainder of the powder will not be ignited; on now allowing air to enter and again heating the wire the powder at once inflames.

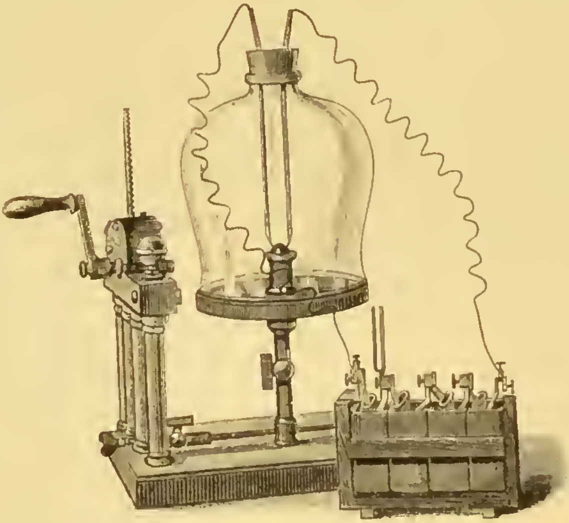

Fig. 50.

The retarding effect of a low barometric pressure on powder fuses is well known; a fuse arranged to burn for 30 seconds will be retarded in its combustion, one second for each inch the mercury of a barometer falls.

The chemical reactions taking place during the combustion of gunpowder are, in the first place, fairly simple, the oxygen of the potassic nitrate converting the carbon into carbon dioxide and carbon monoxide, whilst the nitrogen is liberated and the potassium unites partly with carbon dioxide and oxygen to form potassic carbonate, and partly with sulphur and oxygen to form potassic sulphate, and the following might be taken as the simplest equation representing this principal reaction :—

$$\overset{\text{Saltpetre}}{4(\mathrm{KNO_3})} + \overset{\text{Carbon}}{4\mathrm{C}} + \overset{\text{Sulphur}}{\mathrm{S}} = \overset{\text{Potassic carbonate}}{\mathrm{K_2CO_3}}$$

$$+ \overset{\text{Potassic sulphate}}{\mathrm{K_2SO_4}} + \overset{\text{Carbon dioxide}}{2(\mathrm{CO_2})} + \overset{\text{Carbon monoxide}}{\mathrm{CO}} + \overset{\text{Nitrogen.}}{2\mathrm{N_2}},$$

but this equation does not even approximately represent the proportions in which the ingredients are present in powder, the ordinary service powders having the molecular proportion :—

$$\overset{\text{Saltpetre}}{16(\mathrm{KNO_3})} + \overset{\text{Carbon}}{21\mathrm{C}} + \overset{\text{Sulphur.}}{6\mathrm{S}},$$

whilst the products of combustion obtained, vary with every change in the method of burning ; the pressure under which the combustion takes place, and probably also the size of the charge used, exercising an influence on the products.

Moreover, the powder contains moisture, and the carbon contains hydrogen and oxygen condensed in its pores, and the hydrogen from both these sources plays an important part in the reactions taking place in the breech of a gun, so that to represent the chemical changes taking place by an equation with any degree of accuracy, is an absolute impossibility.

It is probable from the researches of Bunsen and Schischkoff, Linck, Karolyi, Noble and Abel, that during the combustion of gunpowder in the breech of a gun, two distinct stages may be traced.[*]

The first reaction is a process of oxidation occupying a very short space of time and constituting the explosion, during which, as in the previous equation, potassic sulphate, carbonate, carbon dioxide and traces of monoxide, together with nitrogen, are formed. The proportions in which the original ingredients are present, and the proportions of the resulting products showing that the equation must be taken as :—

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[*] Debus, *Phil. Trans.* II, 1882.

Saltpetre.		Carbon.		Sulphur.
$16(KNO_3)$	+	$13C$	+	$5S$

gives

Potassic carbonate		Potassic sulphate		Carbon dioxide		Carbon monoxide		Nitrogen,
$3(K_2CO_3)$	+	$5(K_2SO_4)$	+	$9(CO_2)$	+	CO	+	$8N_2$,

whilst some carbon and sulphur are left unacted upon, and these in the second stage of the action, which goes on whilst the products of the first stage are under great pressure, and at a very high temperature, partly reduce the carbonate and sulphate, with formation of more carbon dioxide and potassic disulphide, according to the equations :—

Potassic carbonate		Sulphur		Potassic sulphate		Potassic disulphide		Carbon dioxide,
$4(K_2CO_3)$	+	$7S$	=	K_2SO_4	+	$3(K_2S_2)$	+	$4(CO_2)$

and

Potassic sulphate		Carbon		Potassic carbonate		Potassic disulphide		Carbon dioxide,
$4(K_2SO_4)$	+	$7C$	=	$2(K_2CO_3)$	+	$2(K_2S_2)$	+	$5(CO^2)$,

during the combustion of the powder also, a small quantity of the sulphur present unites with the metal of the gun, and some also with both the hydrogen occluded in the charcoal, and that liberated by the decomposition of the moisture present in the powder, giving small traces of sulphuretted hydrogen gas, and deducting an atom of sulphur from the equation in order to allow for this secondary action, it is found that the final combustion of the ordinary Service powder can be approximately represented by the equation :—

$$\overset{\text{Saltpetre}}{16(KNO_3)} + \overset{\text{Carbon}}{21C} + \overset{\text{Sulphur}}{5S} =$$

$$\overset{\text{Potassic carbonate}}{5(K_2CO_3)} + \overset{\text{Potassic sulphate}}{K_2SO_4} + \overset{\text{Potassic disulphide}}{2(K_2S_2)} + \overset{\text{Carbon dioxide}}{13(CO_2)} + \overset{\text{Carbon monoxide}}{3(CO)}$$

$$+ \overset{\text{Nitrogen.}}{8N_2}.$$

Using this equation the volume of gas generated by one gram of the powder can be readily calculated.

Saltpetre	$16(KNO_3)$	=	16(101)	=	1616	grams.
Carbon	$21(C)$	=	21(12)	=	252	,,
Sulphur	$5(S)$	=	5(32)	=	160	,,
					2028	grams.

The gaseous products of the combustion are :—

Carbon dioxide	$13(CO_2)$	=	13(22.36) liters	=	290680 c.c
Carbon monoxide	$3(CO)$	=	3(22.36) ,,	=	67080 c.c.
Nitrogen	$8(N_2)$	=	8(22.36) ,,	=	90880 c.c.
					448640 c.c.

2028 grams of powder therefore yield according to this equation, 448640 c.c. of gas measured at 0° C. and 760 m.m. pressure, or 1 gram of the powder yields 221.4 c.c. of gas.

The mean of the results experimentally obtained by Capt. Noble and Sir Frederick Abel for Pebble, R.L.G. and F.G. powders is under these conditions 263.74, the discrepancy between the two being partly due to unavoidable inaccuracies in the equation and probably also to slight experimental errors.

The heat generated at the moment of explosion will, of course, expand this volume of gas to an enormously larger bulk. It has been found that during combustion, 1 gram of powder gave out enough heat to raise 714.5 grams of water from 0° C. to 1° C., that is, gave out out 714.5 thermal units.

The products of combustion of the powder, however, having a much lower specific heat than water, only require approximately .2 the amount of heat to raise them through 1° C., and therefore $\frac{714.5}{.2} = 3572.5°$ C. would be the theoretical temperature attained during the combustion of the 1 gram of powder, and if the explosion were so rapid that no heat could be absorbed by the metal of the gun, and if we assume that the gases at this high temperature, follow the same law of expansion which they do at ordinary temperatures, then as gases expand $\frac{1}{273}$rd of their volume for each °C. increment of temperature, starting from 0° C., we should have—

$$\frac{221.4 \times 3572.5}{273} = 2897 \text{ c.c.}$$

A solid cake of powder (as in a prism) has a density of 1.8, but when a small grain powder is made into a charge, a gram occupies as nearly as possible 1 c.c., the air spaces between the grains taking up the remainder of the space, and when the powder is fired the solid constituents, liquid at the time of explosion or at any rate soon afterwards, occupy one third of the space originally taken up by the powder. If now at the moment of explosion the gases are prevented from expanding, the 2897 c.c. will be compressed into two thirds of a c.c. and would exert a pressure of $2897 \times \frac{3}{2}$ atmospheres $= 4345.5 \times 15$ $= 65172.5$ lb., or 29 tons per square inch. The slowing down of the combustion in the more modern forms of powder prevent any approach to such a pressure as this, because the gradual burning of the charge progressively enlarges the containing space and the metal of the gun abstracts a very considerable amount of heat.

The cocoa powders with their high percentage of saltpetre, low sulphur and large quantities of hydrogen both in charcoal and as moisture have a considerably lower thermal value than the black powders, which also tends to lower the pressure.

From these data we may broadly state that when a black gunpowder is fired, the products of combustion consist of three solids, potassic carbonate, sulphate and disulphide, which form the smoke and fouling of the gun, and of three gases, carbon dioxide, carbon monoxide and nitrogen.

That grain powder gives 270 times its own volume of gas and evolves 714.5 thermal units, which expand the gas to nearly 3,000 times the volume of powder used, and that if the powder is enclosed in a gas tight chamber, this will exert a pressure of nearly 30 tons on the square inch. As has been already pointed out, the composition of the brown or cocoa powder is very different from that of the ordinary black powder, containing considerably more potassic nitrate and a very much smaller percentage of sulphur, whilst the lightly burnt straw charcoal contains considerably larger quantities of hydrogen, and the percentage of water present is also higher.

Captain A. Noble [*] gives the composition of the residue and gases formed during the combustion of cocoa powder under pressure as :—

Solid residue.	
Potassic carbonate...	64.12
Potassic bicarbonate	13.55
Potassic sulphide	none
Potassic sulphate	22.33
	100.00

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[*] *Proc. Inst. Civ. Eng.*, 1884.

Gases.	Volume
Carbon dioxide	51.30
Carbon monoxide	3.42
Hydrogen	3.26
Marsh gas	0.31
Nitrogen	41.71
	100.00

giving at standard temperature and pressure 195 liters of permanent gases, and 837 units of heat* for each kilogram of powder fired.

The larger quantity of water vapour, however, formed during the combustion of the cocoa powder, makes the volume of gas at the moment of explosion practically the same as in the case of black pebble powder.

One kilogram of powder gives at standard temperature and pressure :—

	Black	Cocoa
Permanent gas, liters	295.7	195.4
Water vapour	40.9	122.5
	316.6	317.9

When fired under ordinary atmospheric pressure, the products of combustion are very different; large quantities of potassic nitrite being left undecomposed.

By lowering the percentage of sulphur in the powder, the rate of combustion is made slower, and at the same time a decrease in the volume of permanent gases, and an increase in the heat units evolved follows, and in many powders for sporting and blasting purposes, the reverse action is secured by an increase in the quantity of sulphur present, which, whilst increasing the rapidity of combustion, decreases the amount of heat produced, but gives a larger volume of permanent gases.

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* Kilogram, degree Centigrade.

Many attempts have been made to substitute other oxidising agents for the saltpetre in gunpowder, and of late years, several powders have been made in which ammonic nitrate is employed, and if this could be used successfully it would be of great value, as the compounds of ammonium being either volatile or decomposable at a high temperature, would increase the power of the explosive and at the same time give a practically smokeless powder, but the deliquescent properties of ammonic nitrate are so pronounced, that in a moist atmosphere such a powder would be quickly reduced to the state of mud. Amide powder or Gaen's powder contains :—

Potassic nitrate	101 parts by weight
Ammonic nitrate	80 ,, ,,
Charcoal	40 ,, ,,

whilst the Swiss powder pellets for the Hebler rifles also contain a certain proportion of ammonic nitrate, in the place of some of the saltpetre.

Many other forms of smokeless powder have been proposed and chiefly consist of nitro-cellulose tamed by admixture with various inert substances, or by destruction of the fibrous form ; these will be best considered after guncotton.

CHAPTER XV.

EXPLOSIVES—GUNCOTTON.

History—Cellulose—Action of nitric acid upon cellulose—Collodion cotton—Guncotton—Guncotton an explosive compound and not an explosive mixture—Manufacture of Service guncotton—Precautions to be taken during manufacture—Testing finished guncotton—Properties—Explosion of guncotton by detonation—Wet guncotton—Storage—Products of combustion of guncotton—Force of fired guncotton—Guncotton as a propellant—Nitro-powders—Schultze—E.C.—Johnson-Borland—Engel's—Glaser's—Turpin's—Nobel's.

IN 1838 the French chemist Pélouze drew attention to the fact that when paper was acted upon by the strongest nitric acid it increased in weight and acquired the property of burning with enormous rapidity; whilst as early as 1813 Braconnot had prepared a substance called "xyloidin," by acting upon starch, linen and sawdust in the same way. It was not, however, until 1845 that any serious attention was directed to the use of such substances as explosives, when Schönbein first called attention to nitrated cotton wool and advocated its use as a substitute for gunpowder, showing that in explosive energy it was far superior to it.

Experiments were at once instituted on a large scale and its manufacture carried on in England and also on the Continent, but in 1847 a very serious explosion occurred at the works in which it was manufactured by the Messrs. Hall, at Faversham, whilst a year later an even more serious explosion followed in the guncotton factory at Bouchet, near Paris; and as no reason could be assigned for these and other similar explosions, guncotton was looked upon as too dangerous an explosive for ordinary use and its manufacture was discontinued: a result which was further borne out by the decisions of Committees, appointed by the German and French Governments, which reported against guncotton as an explosive for use in guns. In Austria, however, General Von Lenk continued to experiment upon the causes which had led to the previous disasters and failures, and he succeeded in showing that if the guncotton were entirely freed from every trace of the acids used in its manufacture, it could be stored and kept with perfect safety, and it is also to the same officer that we owe many other important experimental facts connected with this substance to which reference will be made later.

The success of the experiments in Austria attracted attention once more to the subject, and in 1862 the British Association appointed a committee to ascertain all that was known, and to enquire into the possibility of applying guncotton to warlike purposes; much valuable information was obtained by this committee, with which Sir Frederick Abel was associated, and it was he who first introduced the improved processes of manufacture at present employed in the Government factory.

Cotton wool is one of the purest forms of cellulose, or woody fibre ($C_6H_{10}O_5$), which is one of a class of organic compounds called "alcohols," in which one of the atoms of hydrogen in water has been replaced by some group consisting of carbon and hydrogen or carbon, hydrogen and oxygen.

It has been shown, that when potassic hydrate is acted upon by nitric acid, the group of atoms (HO) in the hydrate is replaced by the group (NO_3) contained in the nitric acid, with formation of potassic nitrate and water.

$$\underset{\text{Potassic hydrate}}{K(HO)} + \underset{\text{Nitric acid}}{H(NO_3)} = \underset{\text{Potassic nitrate}}{K(NO_3)} + \underset{\text{Water.}}{H(HO).}$$

And in the same way when a small portion of cotton wool is acted upon by the strongest nitric acid, the group (HO) in the cellulose is replaced by the (NO_3) group from the nitric acid with the simultaneous formation of water.

$$\overset{\text{Cellulose}}{C_6H_7O_2(HO)_3} + \overset{\text{Nitric acid}}{3(HNO_3)} = \overset{\text{Guncotton}}{C_6H_7O_2(NO_3)_3} + \overset{\text{Water.}}{3(H_2O)}.$$

If guncotton were made on the large scale in this manner, the water formed during the action would dilute the nitric acid, and would give rise to an inferior kind of guncotton called collodion cotton, in which only two thirds of the (HO) groups contained in the cellulose would be replaced by (NO_3).

$$\overset{\text{Cellulose}}{C_6H_7O_2(HO)_3} + \overset{\text{Nitric acid}}{2(HNO_3)} = \overset{\text{Collodion cotton}}{C_6H_7O_2(HO)(NO_3)_2} + \overset{\text{Water.}}{2(H_2O)}.$$

And in order to prevent this dilution taking place, the strongest nitric acid is mixed with 2½ times its own volume of strong sulphuric acid, which, having a strong affinity for water absorbs it as fast as it is formed and so maintains the nitric acid at its original strength.

Accepting the formula $C_6H_7O_2(NO_3)_3$ as representing guncotton, it is seen that the group (NO_3) is the oxidising portion of the molecule, just as in gunpowder the (NO_3) contained in the potassic nitrate (KNO_3) supplied the oxygen necessary for the combustion of the charcoal and sulphur; but a wide difference exists between the two explosives: in gunpowder we have merely a mechanical mixture of the combustibles and the store of oxygen; when the powder is fired the saltpetre must be resolved into its constituents, and from these and the charcoal and sulphur, the new solids and gases forming the products of explosion are built up. Whilst in the case of guncotton, the combustibles and store of oxygen are both present in the same molecule, and by a simple rearrangement, split up into the simpler molecules, carbon dioxide and monoxide, hydrogen and nitrogen. Gunpowder is an explosive mixture, whilst guncotton is an explosive compound.

In the manufacture of guncotton for Service use as practised at Waltham Abbey, the best white cotton waste only is used, and is supplied free from all grease and dirt (which has previously been extracted by boiling it with dilute alkaline solutions); this is an important operation, as if any greasy or resinous substances remained in the cotton, they would form compounds with the acids employed, which would be liable to cause decomposition.

The cotton is first picked over by hand, all foreign substances being removed, and it is then passed through the "teasing machine," in which rollers bearing iron teeth rotate and tear up any knots or lumps which exist in the waste; after this it is passed through the "cutting machine," which chops it into pieces not exceeding 2 inches in length. If any moisture were present in the waste it would cause evolution of heat on dipping in the acids, the cotton is therefore next dried by passing it through a chamber heated to about 83° C., in which the cotton placed on endless bands travels backwards and forwards for about 20 minutes; it is then weighed up into lots of $1\frac{1}{4}$ lb. called a charge, and is placed in an airtight box to keep it dry until it has cooled down and is ready for dipping.

The mixture of acids consists of one part by weight of nitric acid of specific gravity 1.52, to 3 parts by weight or 2.45 by volume of sulphuric acid of specific gravity 1.84; these are run in the right proportions into a mixing tank fitted with a lid, through an opening in which they can be thoroughly mixed by means of a stirrer, worked backwards and forwards for some minutes. Mixing the acids is attended by evolution of a considerable amount of heat and the mixture is allowed to stand until thoroughly cool, when it is run into the dipping pan, a small cast iron tank holding about 220 lb. of the mixed acids and surrounded on the outside by running water, in order to guard against rise of temperature during the formation of the guncotton, which would tend to increase the percentage of collodion cotton present in the finished product.

The charge of 1¼ lb. of dry cotton is now taken from its tin, and is stirred as quickly as possible into the mixed acids, in which it is allowed to remain for five or six minutes, it is then lifted on to a perforated shelf at one end of the dipping pan, and the large excess of acids squeezed out by a plate worked by a lever. The 1¼ lb. of cotton which has absorbed 14 lb. of acids is now transferred to an earthenware pot fitted with a cover, the pot being placed in running water to prevent any rise in temperature, and the charge remains under these conditions for upwards of 24 hours, when the excess of acids present completes the conversion of the cotton. The next step is to get rid of the free acids which are still present in quantity. To do this the contents of six pots are transferred to a centrifugal machine, consisting of a perforated iron cylinder made to rotate at the rate of 1,200 revolutions per minute: about ten pounds of acids being in this way separated from each charge of cotton.

The converted cotton is now placed in the hopper of the "immersing machine" where a paddle wheel rapidly plunges it beneath a stream of water, and passes it on into a cistern where it is kept continually stirred in running water until it no longer tastes acid to the tongue. The guncotton is now again wrung out in a centrifugal machine and is then boiled for two periods of eight hours each in wooden tanks, into the water in which steam is blown; after each boiling the water is wrung out as before, and finally the guncotton should be so far free from acid that it does not redden blue litmus. The guncotton is now reduced to a pulp in a machine of the same construction as a paper maker's "hollander," in which the fibre suspended in water is made to continually pass between a bed plate and a roller, both being armed with knives, and after being pulped for five hours, is reduced to a very fine state of division, and then passes through a pipe into the "poaching machine," another large oval tank in which paddle wheels keep the pulp constantly agitated with a large volume of fresh water, which, owing to the fine state of division of the pulp, thoroughly washes every portion of it. After six hours in the poacher samples of the pulp are tested, and if the requirements of the tests are satisfied, enough lime water, whiting and caustic soda (sodic hydrate), are mixed with it to leave between one and two per cent. of free alkali in the finished guncotton. The pulp is now drawn up by means of a vacuum pump into an iron reservoir, called the "stuff chest," in which revolving arms keep the pulp from settling, and from which measured quantities can be run off into the moulds, the bottoms of which are made of very fine wire gauze, which allows the water to pass through, but keeps back the fine pulp, the filtration being aided by the action of a partial vacuum maintained below the moulds.

When most of the water has been in this way separated, hydraulic pressure of about 34 lb. on the square inch, is brought to bear upon the semi-solid pulp, which expels a large proportion of the remaining water, and renders the blocks sufficiently hard to bear careful handling. The moulded guncotton is now taken to the "press house" where it is subjected to hydraulic pressure of about five tons on the square inch, which reduces it to one third of its original bulk, making it so hard that it does not perceptibly yield to the pressure of the finger, and when dry will just sink in water.

During the process of manufacturing guncotton, every precaution is taken to prevent any rise of temperature during the period when the cotton is in contact with free acid, in order to avoid decomposition of the guncotton, with evolution of large quantities of red fumes (oxides of nitrogen), and the formation of oxalic acid and other products, whilst even a small rise of temperature increases the proportion of collodion cotton present, and so detracts from the value of the finished product. In the second stage of the manufacture—from the removal of the superfluous acid in the centrifugal wringing machine to the moulding of the blocks, the object of all the operations is to thoroughly free the converted fibre from every trace of free acid, and it has been conclusively proved that it was to a great extent owing to retention of free acid that the explosions which attended the early manufacture of guncotton were due. Cotton when examined under the microscope is seen to consist of minute tubes, which, during immersion in the mixed acids, become filled with them, and the last traces cannot be removed by any ordinary rinsing process such as was at first considered sufficient, and when such impure guncotton is packed in cases, chemical action is maintained by the traces of acid present, the heat generated being confined to the centre of the mass by the nonconductive properties of the wool surrounding it; this action increases very rapidly with the rise of temperature, and a temperature is soon reached at which the guncotton catches fire. The liability to spontaneous decomposition is much increased when wool which has not been thoroughly cleansed, or which contains any fatty or resinous matter is used, and also by the presence of a large proportion of collodion cotton which is not so stable as the completely nitrated product.

This action was still further favoured in the guncotton first manufactured by its not being left long enough in contact with the acids, so that complete conversion of the whole of the cotton had not taken place and some less stable products were present.

The finished guncotton is tested at Waltham Abbey and the amount of alkalinity determined; the alkaline matter present should not be less than 0.5 per cent. and should not exceed 2.0 per cent.

Having tested the finished guncotton for alkaline matter, it is dried at a low temperature and tested for evolution of acid. This is done by taking a small portion of the finely divided substance and placing it in a test tube with a piece of test paper moistened with a mixture of potassic iodide and starch, and then gently heating the tube in a water bath at a temperature of 66° C. No discolouration of the paper must take place for at least ten minutes. If there is any free acid present, nitrous fumes will be evolved which will attack the potassic iodide, liberating iodine, which at once gives an indication by forming the blue iodide of starch.

The percentage of collodion cotton present is next determined by treating a carefully weighed sample of the guncotton for some hours with a mixture of ether and alcohol, which dissolves the collodion cotton but not the fully nitrated product. When fifty grains of the guncotton are treated in this way for three hours, with frequent shaking, with four ounces of a mixture of two parts by volume of ether to one volume of alcohol, the loss of weight due to collodion cotton dissolved out from it, should be very small.

Unconverted cotton can be detected by treating the guncotton with acetic ether, which dissolves the converted but not the unconverted cotton fibre.

Guncotton differs very widely from gunpowder in its properties, requiring a much lower temperature for its ignition, as gunpowder has to be heated to a temperature of at least 316° C., whilst guncotton will often take fire at 136° C., and invariably does so below 204° C. Guncotton can be detonated by striking it with a steel hammer on an anvil; the explosion however is confined to the portion struck; but it is very difficult, if not impossible, to ignite powder in this way. The rate at which guncotton burns is dependent upon the mode of its ignition and the conditions under which it is placed. A piece of loose guncotton placed on the hand and touched with a hot glass rod, burns away so rapidly that the skin is not scorched or burnt. For the same reason a piece of guncotton can be fired upon a small pile of gunpowder without igniting the powder; and grains of powder can indeed be wrapped up in guncotton and the guncotton ignited without the powder being burnt.

Rapid as this combustion is, however, it occupies an appreciable time, as may be seen by igniting a train of guncotton, which takes several seconds to burn away, giving at the same time a large flame. If guncotton be confined at the moment of ignition, this flame is forced back into the mass, and by rapidly heating it, brings it to the point at which combustion passes into explosion; and prior to 1868, when guncotton was required for destructive purposes, it was always confined in strong cases; but in that year, Mr. E. O. Brown, of Woolwich, discovered that when a detonating fuze was exploded in contact with guncotton, the unconfined mass at once exploded with enormous violence: and this discovery of the possibility of detonating guncotton, marks the second great stage in the history of the substance.

The fact that certain unstable compounds could be caused to undergo instantaneous decomposition by the sympathetic vibration set up in them by a sharp explosion, either in contact with or close to them, had been previously known, and Nobel had exploded nitro-glycerin by detonation some years previously, but another new and most important fact was discovered nearly at the same time, namely: that guncotton when wet and containing 15 to 20 per cent. of water, could be detonated and gave just as good results as when dry, provided that a small proportion of dry guncotton were placed in contact with the detonating fuse, the explosion of this portion ensuring the detonation of the wet mass.

The great importance of this discovery is seen when one considers that the sudden conversion of the solid mass into gaseous constituents, endows guncotton when exploded in this way, with an enormous destructive power which is as great when the explosive is free as when it is confined, and that, although it can be detonated when wet, that in this condition it is uninflammable, and that a hole may be bored through a block of wet guncotton with a red hot iron without inflaming it, a fact which renders it the safest explosive we possess, as it can be stored wet in airtight vessels and dried as it is required for use, or even used wet with a small primer of the dried guncotton.

The non explosive properties of wet guncotton, under all ordinary conditions, were demonstrated by the Government Committee of 1871, who constructed two small magazines, and in one placed a securely fastened tank containing 2,240 lb. of guncotton in disks; whilst in the second magazine the same amount was packed in eighty closed boxes (28 lb. in each): in both cases the guncotton contained about 30 parts of water to 100 of the dry material. The remaining space in the magazines was now filled with shavings and other inflammable materials, which were fired; in two hours the entire contents had burnt away, but without the slightest sign of explosion, although the heat generated was very great as was shown by the distortion of iron bars upon which the cases had rested.

If dry compressed guncotton is ignited by touching it with a hot rod, it burns away with a fierce flame but without explosion, but if larger quantities were ignited in this way the portions first burning would quickly heat up other parts of the mass to the temperature at which combustion becomes explosively rapid, and as soon as this point was reached detonation of the whole mass would take place.

The great increase in effect gained by detonating such explosives as guncotton arises from the enormous increase in rapidity of explosion. A train of ordinary guncotton fired by a hot rod takes several seconds to burn a distance of a few feet, but if a train of compressed guncotton were fired by detonation, the explosion would travel at the rate of 200 miles a minute. When guncotton is fired by touching it with a red hot rod its combustion occupies an appreciable time, and the gaseous products evolved have time to find space for themselves in the surrounding air. If, however, detonation be employed, the conversion of the solid into an enormously increased volume of gas takes place instantaneously and the atmospheric pressure forms just as good a "tamping" for the guncotton as the strong metal cases which were employed before the principle of detonation was recognised.

In order to detonate guncotton, fuses charged with mercuric fulminate are now generally used.

The products formed during the explosion of guncotton vary so greatly with the conditions under which it is fired and the proportion of collodion cotton present, that any attempt to construct an equation must be misleading.

When guncotton is fired under ordinary atmospheric pressure, the products of combustion are found to be carbon dioxide, carbon monoxide, marsh gas, nitric oxide, nitrogen, water vapour and sometimes traces of cyanogen and hydrocyanic acid; but as the rapidity of explosion and the pressure increase, so the products become less complex, and it is not at all improbable that under the conditions of temperature existing during rapid explosion in a confined space, the reaction which takes place with fully nitrated cotton is:—

$$\overset{\text{Guncotton}}{C_6H_7O_2(NO_3)_3} = \overset{\text{Carbon dioxide}}{5CO_2} + \overset{\text{Carbon monoxide}}{CO} + \overset{\text{Hydrogen}}{H_7} + \overset{\text{Nitrogen.}}{N_3},$$

an equation which would give 870 c.c. of gas at normal temperature and pressure, an amount in excess of that found by actual experiment, which gives 750 c.c., and an evolution of heat equal to 1,056 thermal units.

Estimations of the pressure developed by the detonation of guncotton differ greatly in value, Berthelot placing it as high as 24,000 atmospheres, or 160 tons per square inch; whilst other authorities estimated it as not much more than half this pressure.

The fact that all the products of the explosion of guncotton are gaseous renders it smokeless, whilst the rapidity of its combustion would prevent much heating of the metal of guns if it were used for artillery, and for these reasons many attempts have been made to utilise it for this purpose; but as a propellant, its use up to the present time has been a failure in anything but small arms.

It has been shown that the compression of guncotton causes it to burn much more slowly when merely ignited under ordinary atmospheric conditions, and it was in this direction that all the early experiments tended, but it was soon found that in the chamber of a gun the pressure forced the flame first formed into the interior of the mass and produced detonation, which giving no time for overcoming the *vis inertia* of the projectile, threw an enormous strain on the gun and gave very unsatisfactory muzzle velocities. Many attempts have also been made to so dilute and tame the guncotton by admixture with inert or less explosive bodies as to render it sufficiently slow for this purpose, and several powders made on this principle are in the market, but none of them can be advantageously used for anything above the size of a rifle.

The "Turpin" smokeless powder, patented in 1888, consists of guncotton partly dissolved in a mixture of acetone and ether which already has had collodion cotton dissolved in it; the pasty mass so obtained is cast into sheets and passed between rollers to compress it, and is, when dry, cut and cross cut into small grains or cubes of the required size.

"Engel's" powder, patented in April, 1887, consists of nitrated cellulose, or any form of vegetable fibre, which is worked into a semi-gelatinous mass with acetone or acetic ether, and then mixed with some oxidising substance like the nitrate or chlorate of potassium or barium, and the mass cast into cakes, which are then granulated to the required size. Such a powder, however, cannot be smokeless on account of the presence of the metallic salts.

"Glaser's" powder consists of paper, nitrated in the usual way, and then partly gelatinised by the use of acetone or other solvent.

"Nobel's" powder, patented in 1888, consists of nitrated cotton and camphor dissolved in nitro-glycerin, and cast and granulated to the required size, a volatile solvent like benzol being used in the manufacture to aid solution, and this is afterwards evaporated off, leaving a horny mass behind.

Amongst the older forms of nitro-cellulose powders, are Schultze's powder, consisting of nitrated sawdust; the E.C. sporting and rifle powders, consisting of nitrated cotton mixed with nitrates of barium and potassium, and waterproofed with resinous or waxy substances; these powders, however, give a certain amount of smoke, as is also the case with the Johnson-Borland powder, which consists of collodion cotton, mixed with nitrates and carbonaceous matter and made into pellets which are then saturated with a solution of camphor in light petroleum or benzoline, which being evaporated off leaves the camphor intimately mixed with the other constituents, and if the mass is now heated in a closed vessel at 100° C., and the camphor afterwards distilled off, the mass is found to have been hardened throughout by the action of the camphor.

Some of these powders give very good results, but doubt is felt as to their keeping in hot climates without undergoing change; indeed, it is stated that a powder of this description, used in the French Lebel rifle (poudre B), gave such unsatisfactory results after keeping, that a return to the black powder was decided upon.

CHAPTER XVI.

EXPLOSIVES—(*concluded*).

Nitro-glycerin—Dynamite—Nitro-glycerin mixtures—Carbolic acid—Picric acid and the picrates—Picric powder—Mélinite—Lenite—Sprengel explosives—Roburite—The fulminates—Preparation and properties of mercuric fulminate—Detonation.

IN 1847, Sobrero whilst experimenting with glycerin, found that by treating this substance with strong nitric acid he obtained a compound which, on account of its exploding on a sudden rise of temperature, he called "pyro-glycerin," but its value as an explosive was not realised until 1863, when Alfred Nobel showed that by firing it by detonation an excessively powerful effect could be obtained.

Glycerin or glycerol ($C_3H_8O_3$) is a sweet syrupy liquid, having a specific gravity of 1.269 and a boiling point of 290° C., at which temperature, however, it undergoes partial decomposition; it is soluble in water and in alcohol, but is insoluble in ether. It is contained in the liquor left after the separation of soap in the manufacture of that article, being one of the products formed when oils or fats are acted upon by alkalis, and is obtained in still larger quantities during the manufacture of palmitic acid for candle making.

The vegetable fat, palm oil, which chiefly consists of palmitin, when acted upon by superheated steam, is broken up into palmitic acid and glycerin which can afterwards be separated.

$$\overset{\text{Palmitin}}{C_3H_5(C_{16}H_{31}O_2)_3} + \overset{\text{Steam}}{3(H_2O)} = \overset{\text{Palmitic acid}}{3H(C_{16}H_{31}O_2)} + \overset{\text{Glycerin.}}{C_3H_5(HO)_3}.$$

When acted upon by strong nitric acid, glycerin, like cellulose, is converted into a nitrate with simultaneous formation of water.

$$\overset{\text{Glycerin}}{C_3H_5(HO)_3} + \overset{\text{Nitric acid}}{3(HNO_3)} = \overset{\text{Nitro-glycerin}}{C_3H_5(NO_3)_3} + \overset{\text{Water.}}{3(H_2O)}.$$

In making nitro-glycerin, nitric acid having a specific gravity of 1.48 is mixed with twice its weight of concentrated sulphuric acid specific gravity 1.84, which is placed in stone jars containing about 7 lb. each, and these are stood in running water, so as to keep the temperature as low as possible, and about a pound of glycerin of specific gravity of 1.25 is cautiously stirred into the contents of each jar, care being taken that the temperature does not rise above 25° C. The glycerin dissolves in the strong acids and after standing for from 15 minutes to half an hour, the mixture is poured in a very thin stream into about 6 gallons of water which is agitated to avoid rise of temperature. This dilution causes the separation of nitro-glycerin in small oily drops, which sink to the bottom of the vessel, and the oil is then thoroughly washed by agitating it in running water until free from every trace of free acid; a little free alkali being put in to the last wash water and sometimes a trace of magnesia added to the finished product, to guard against the liberation of any trace of acid on decomposition.

Nitro-glycerin so prepared is an oily colourless liquid, which has no odour and is insoluble in water, although it readily dissolves in ether, benzol, wood spirit and hot alcohol, and from the solution so formed can again be precipitated on dilution with water.

It has a violent effect upon the system, acting in large doses like strychnine, whilst even traces produce vertigo, and as it is absorbed through the skin, people working with it are frequently at first seriously affected, but after a time, experience no ill effects and, it is said, present a more than usually healthy appearance. When cautiously heated to 185° C. it boils and emits red fumes, it burns briskly at 217° C. and detonates at 257° C. When a lighted match is applied to it, it burns quietly away and when the light is removed the flame generally goes out; indeed, a lighted match may be extinguished by plunging it into nitro-glycerin It is, however, detonated by a sudden blow or by heating it to 257° C. Nitro-glycerin becomes solid at 4° C., and in this condition is comparatively inert, hence it is necessary to thaw it before use, an operation attended with considerable risk. It is stated that exposure to the direct rays of the sun will convert it into a very unstable and explosive substance, and also that the presence of ozone will sometimes cause its spontaneous decomposition.

When nitro-glycerin is exploded, it is instantaneously decomposed into gaseous products, the probable decomposition being:—

$$\overset{\text{Nitro-glycerin.}}{2\left(C_3H_5(NO_3)_3\right)} = \overset{\text{Carbon dioxide}}{6(CO_2)} + \overset{\text{Water}}{5(H_2O)} + \overset{\text{Nitric oxide.}}{NO} + \overset{\text{Nitrogen.}}{N_5}.$$

Showing that the amount of oxygen present is more than sufficient for complete combustion, which is not the case in any other explosive compound.

Nobel calculates that about 1,200 times its own volume of gas, calculated at normal temperature and pressure, is generated by the explosion of nitro-glycerin, whilst the heat evolved expands it to nearly eight times this volume; its explosive force, volume for volume, being nearly thirteen times as great as gunpowder.

The rapidity of detonation of nitro-glycerin is very great, and it is this which gives rise to the downward effects noticeable in all nitro-glycerin or dynamite explosions.

Six cubic inches of nitro-glycerin, when exploded, would yield about a cubic yard of gas, and would require, approximately, $\frac{1}{40000}$th of a second for conversion into the gaseous form. A square yard of surface carries an atmospheric pressure of, roughly, nine tons, so that the gaseous products would have to lift nine tons to a height of one yard in $\frac{1}{40000}$th of a second, and the earth being rigid, is broken up by the recoil from this enormous strain.

For blasting purposes nitro-glycerin was at one time very extensively used; the fact of its being unaffected by moisture gave it a great advantage, whilst the rapidity of its explosion made it only necessary to prepare a bore hole, partly fill it with nitro-glycerin and then fill up the hole with water; the water forming just as good a tamping for the nitro-glycerin when fired by detonation as if the hole had been plugged with wood or metal. The use of nitro-glycerin for blasting purposes is, however, attended with several inconveniences, as, being fluid, it can only be used in downward bore holes, whilst its transport in the liquid form has given rise to many accidents; and, finally, the liquid state is not very suitable for detonation as the fluid yields to the sudden blow, and is often scattered instead of being completely exploded, so reducing its power, and becoming a source of danger in subsequent operations. In order to avoid these drawbacks, Nobel made the nitro-glycerin into certain plastic preparations by mixing it with various absorbent substances, and these mixtures, in many cases, have a higher explosive power than nitro-glycerin itself.

Dynamite consists of nitro-glycerin absorbed by a porous, siliceous earth called Kieselgühr, which is found in deposits at Oberlohe in Hanover, and which is free from grit. Having been heated in contact with air to get rid of as much of the organic matter as possible, it is mixed, when cold, with the nitro-glycerin in wooden troughs, and absorbs from 70 to 75 per cent. of it. Many other substances have been from time to time employed as a vehicle for the nitro-glycerin; some of them inert substances, like Kieselgühr, sugar, alumina, magnesia and the ashes of plants, which require a considerable percentage of the nitro-glycerin to be mixed with them; whilst others, like guncotton, mixtures of combustible and oxidising salts, do not need so large a quantity to make them effective explosives.

Tutonite and Forcite—forms of dynamite with varying proportions of nitro-glycerin.

Lithofracteur, Vigorite and Vulcan powder are nitro-glycerin absorbed by mixtures of sodic nitrate, sulphur, carbon, or sawdust, and sometimes a small percentage of Kieselgühr.

Blasting gelatine No. 1 consists of equal parts of guncotton and collodion cotton, saturated with nitro-glycerin which gelatinises them. This is perhaps the most powerful explosive known, for whilst in guncotton there is a deficiency in the quantity of oxygen present, the excess in the nitro-glycerin supplies the deficiency and the result is that nearly complete combustion of all the ingredients is obtained.

Blasting gelatine No. 2 consists of No. 1 mixed with potassic nitrate and finely divided carbon.

Glyoxylin and Atlas powders consist of nitro-glycerin absorbed by nitrated guncotton and rendered waterproof by a small quantity of paraffin.

Dualin and Petrolite are chiefly composed of nitro-glycerin absorbed by sawdust.

Nitro-magnite is magnesia saturated with nitro-glycerin.

Dynamite No. 2 is practically gunpowder in which the sulphur has been replaced by nitro-glycerin, whilst Rendrock, Mica powder, Hercules powder and Electric powder are all forms of dynamite varying in little else but name and the proportions of their ingredients.

The increase in explosive force gained by the rigidity of form in these mixtures, is shown by the following table, in which the work done by equal weights of these explosives is compared with nitro-glycerin.

Name of Explosive.	Work done in a horizontal direction compared with nitro-glycerin = 100.	Percentage of Nitro-glycerin.
Blasting gelatine	144	89
Hercules powder No. 1	130	42
Dynamite No. 1	123	75
Rendrock	117	60
Hercules powder No. 2	102	42
Dynamite No. 2	102	36
Mica powder No. 1	102	52
Vulcan powder No. 2	101	35
Nitro-glycerin	100	100
Vulcan powder No. 1	96	30
Electric powder No. 1	85	33
Electric powder No. 2	76	28
Mica powder No. 2	76	40

Phenol, or carbolic acid (C_6H_5HO), is one of the compounds obtained from heavy tar oil, and is much used as a constituent of disinfecting powders and liquids. It crystallises in needle shaped crystals possessing a strong tarry smell, and has a fusing point of 42° C., the liquid boiling at 182° C., and when a small quantity of the fused acid is poured into nitric acid, a violent action takes place with evolution of red fumes ; when this action has moderated, some of the strongest nitric acid is added and the liquid boiled until red fumes nearly cease to be evolved, and on cooling, a yellow substance called picric acid crystallises out, and can be purified by recrystallising from water.

The change which takes place during the action of the nitric acid upon the carbolic acid may be represented as follows :—

$$\overset{\text{Phenol}}{C_6H_5OH} + \overset{\text{Nitric acid}}{3(HNO_3)} = \overset{\text{Picric acid}}{C_6H_2(NO_2)_3OH}$$
$$+ \overset{\text{Water.}}{3(H_2O)}.$$

Picric acid may be regarded as a nitro-substitution product, in which three atoms of the hydrogen in the original phenol are replaced by the radicle (NO_2), and by the action of picric acid on metals or metallic bases, is obtained the class of salts known as picrates—

$$\overset{\text{Picric acid}}{C_6H_2(NO_2)_3OH} + \overset{\text{Potasaic hydrate}}{KHO} = \overset{\text{Potassic picrate}}{C_6H_2(NO_2)_3OK}$$
$$+ \overset{\text{Water.}}{H_2O},$$

many of which salts have the property of exploding when heated or struck.

Picric acid is a pale yellow crystalline solid, having the form of plates or prisms, and being but little soluble in cold water, although readily soluble in alcohol. It derives its name from its intensely bitter taste, and for this reason has been used in some hop substitutes for bitter ales. It is extensively used as a dye for silk and wool, which it colours a fast yellow.

On heating the crystals of picric acid they fuse at 122° C. with partial sublimation and explode at a slightly higher temperature.

When exploded, the decomposition is somewhat complicated. Nitrogen, carbon dioxide, carbon monoxide, nitric oxide, water vapour and hydrocyanic acid are produced, and a residue of unburnt carbon left behind; and inspection of the formula for picric acid makes it at once evident that there is not nearly enough oxygen for the complete combustion of the carbon and hydrogen present, and for this reason nearly all the picric powders and explosives consist of mixtures of picric acid or its salts, with oxidising substances of a character suitable for supplying this deficiency.

It is nearly twenty years ago since Désignolle first introduced mixtures of potassic picrate and saltpetre for use as bursting charges for torpedoes and shells, and this was improved upon by Sir Frederick Abel, who substituted ammonic picrate for the potassium salt, the same composition also being adopted in Brugère's picric powder. Soon after this Dr. Sprengel* showed that picric acid by itself was capable of being detonated by mercuric fulminate, and in 1885 E. Turpin patented the use of picric acid for shells and torpedoes, and proposed to make it less sensitive to percussion by melting it and pouring it whilst hot into the shells, or by making the grains into a solid mass by means of collodion, and in this way a very great weight of the explosive can be got into a small space on account of the high specific gravity of the fused mass.

Mélinite contains picric acid as its chief constituent, mixed with some oxidising substance, or as stated by some authorities, merely made into a compact mass with collodion, and the explosive "Lenite" is practically the same substance.

Other tar products besides phenol can be made to yield nitro-substitution products, some of which, like trinitro-cresol (crésilite) or the nitro-benzols can be employed as explosives *per se*, or as constituents of explosive mixtures such as Securite or Bellite.

In the explosives so far considered, gunpowder alone can be used as a propellant for the discharge of projectiles from large guns, whilst for rifles and small machine guns, certain preparations of guncotton will probably soon be used, but the remainder of the explosives are only of use for charging shells and torpedoes, destroying palisades, clearing wrecks, disabling guns and mining operations, and for this latter class of work, the explosive must be carefully selected with regard to the work which has to be done.

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* 1873.

If large masses of coal, slate or building stone are to be detached, then blasting powders are far superior to any of the higher explosives such as guncotton, nitro-glycerin or its mixtures, whilst if shattering effect is desired, for tunnelling through a hard material or other operations of this kind, then the latter class of explosives is the best.

In 1873, Dr. Sprengel[*] pointed out that in many of the existing explosives, the proportions between the combustible and the supporter of combustion were not such as to give the highest explosive value, and he suggested that not only would safety of storage and transport be ensured, but also higher explosive values could be obtained by employing mixtures of two solids, a solid and a liquid, or of two liquids, one of which should be a hydrocarbon containing the elements carbon and hydrogen in a condition favourable to their rapid combination with oxygen, whilst the second should be an easily decomposable compound rich in oxygen, that could be made available for the combustion of the hydrocarbon and which should be mixed with it, in the proportions required to give the highest explosive value, when required for use. And he showed that mixtures of potassic chlorate with such bodies as benzene, petroleum, and phenol, could be detonated and exploded with great violence.

This class of explosives, named after the inventor "Sprengel explosives," is used to a considerable extent for blasting and engineering purposes. The principle are:—

Rack-a-rock—which obtained notoriety from being the explosive used in the Hellgate explosions, when the rocks at the mouth of New York Harbour were destroyed—which consists of cartridges of potassic chlorate saturated with a liquid hydrocarbon, or in some cases nitrobenzol, before using.

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[*] Sprengel 'On a new class of Explosives,' *Chem. Soc. Journal*, 1873, p. 796.

Panclastite.—This name was adopted by M. Turpin, in 1885, for a class of explosives which contain liquid nitrogen tetroxide as the oxidising agent, confined in a glass vessel which, when broken, ensures contact with the combustible consisting generally of petroleum, benzol, ether, bisulphide of carbon or volatile hydrocarbon.

M. Turpin claims the idea as original, but it is hard to see on what grounds, as liquid nitrogen tetroxide was one of the oxidising agents specially mentioned by Dr. Sprengel in his original memoir.

Hellhoffite is a mixture of nitrated tar oils or petroleum, mixed when wanted for use, with the strongest acid.

It has been proposed* to construct shells in which nitrated benzol and nitric acid are placed in separate compartments and are mechanically mixed during the flight of the shell through the air, the mixture then becoming explosive.

Oxonite consists of a picric acid cartridge containing a glass vessel with the strongest nitric acid sealed up in it; this is broken by a blow from a hammer before the cartridge is used, so as to allow the constituents to mix.

Roburite.—In this explosive, benzol (C_6H_6) has two atoms of its hydrogen replaced by the NO_2 radicle, and another atom by chlorine, forming a compound called dinitro-chlorbenzol $C_6H_3\,Cl(NO_2)_2$, and this compound is mixed either when wanted for use or shortly before with ammonic nitrate (NH_4NO_3), the hygroscopic properties of which are overcome by waterproofing it with a small quantity of paraffin.

This mixture can only be exploded by an especially powerful fuse, and its inventor, Dr. Carl Roth, claims that the decomposition then takes place according to the equation :—

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* Grüson.

$$\overset{\text{Dinitro-chlorbenzol}}{C_6H_3Cl(NO_2)_2} + \overset{\text{Ammonic nitrate}}{9(NH_4NO_3)}$$

$$= \overset{\text{Carbon dioxide}}{6(CO_2)} + \overset{\text{Water vapour}}{19(H_2O)} + \overset{\text{Nitrogen}}{10N_2} + \overset{\text{Hydrochloric acid.}}{HCl},$$

and that no flame is given off during explosion which could ignite firedamp, and that the fouling of the air of the mine is much less than in the case of other blasting compounds.

Nearly all the explosives are now fired by means of a cap, detonator, or fuse, charged with one of a class of bodies called fulminates, or mixtures in which they play an important part, and the fulminate generally used is mercuric fulminate ($HgC_2N_2O_2$), made by acting upon mercury with nitric acid and alcohol. It may be made on a small scale by dissolving 3 grams of mercury in 36 grams (27.7 c.c.) of nitric acid having a specific gravity of 1.36; as soon as it is all dissolved and whilst the solution still is yellow from presence of nitrous fumes, take 34.5 grams (43 c.c.) of 90 per cent. alcohol and add one half; a violent action takes place and when this ceases, the second portion of alcohol is added and the mixture allowed to stand, when the mercuric fulminate crystallises out in small needleshaped crystals which have a greyish colour from the presence of a trace of free mercury.

When made on a large scale the operation is a little different, the mercury being dissolved in the nitric acid and the solution allowed to cool, the alcohol is then added in one operation, which is carried out in an open shed, in a large retort and the escaping fumes condensed and utilised. The fulminate so obtained is well washed with distilled or rain water, until free from all acid, and is stored whilst still containing 20 per cent. of moisture.

The changes taking place during the formation of mercuric fulminate are not very thoroughly understood, but the general action may be looked upon as resulting in the solution of mercury in nitric acid with the production of mercuric nitrate and nitrous acid, and the interaction of these with the alcohol :—

$$\underset{\text{Mercuric nitrate}}{Hg(NO_3)_2} + \underset{\text{Nitrous acid}}{2(HNO_2)} + \underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Mercuric fulminate}}{HgC_2N_2O_2} + \underset{\text{Water}}{3(H_2O)} + \underset{\text{Nitric acid.}}{2(HNO_3)}.^*$$

Mercuric fulminate is very heavy, having a specific gravity of 4.4 and it is easily detonated either by a blow, by friction, by touching it with a wire heated to 190° C., by an electric spark or by contact with strong sulphuric or nitric acids, when it is instantaneously decomposed into—

$$\underset{\text{Mercuric fulminate}}{HgC_2N_2O_2} = \underset{\text{Mercury}}{Hg} + \underset{\text{Carbon monoxide}}{2(CO)} + \underset{\text{Nitrogen.}}{N_2}$$

with a sharp flash and evolution of greyish fumes of mercury. The rapidity of its explosion is so great, that, when exploded in contact with any easily decomposable body, the vibration which it sets up travels through the mass with the rapidity of sound and affects the whole almost instantaneously, giving rise in many cases to the most rapid form of explosion known as detonation. Berthelot has shown that even stable gases such as nitrogen dioxide can be decomposed into their elementary constituents by the detonation of mercuric fulminate.

This rapidity of explosion causes the local effects of the detonation to be very great, but the effect at a distance is much smaller than that of such an explosive as gunpowder. On explosion, mercuric fulminate gives 1304 times its own volume of gas measured at normal temperature and pressure, whilst the 403 units of heat evolved, expand this volume enormously, and it has been calculated that the pressure generated at the moment of explosion is about 48,000 atmospheres.

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* *Bloxam*, p. 626.

If a small train of mercuric fulminate is laid on a metal plate and some gunpowder is placed on it and the fulminate fired, the powder will be scattered but not ignited, the explosion being too rapid to communicate itself to the powder; if, however, a little finely powdered chlorate of potash is mixed with the fulminate, the flame will be increased and the powder ignited. This can be explained when it is considered that carbon monoxide, which is evolved by the decomposition of the fulminate, is oxidised to carbon dioxide by the oxygen from the chlorate, thus increasing the flame and the temperature.

Advantage is taken of this fact in the preparation of composition for percussion caps for military purposes, in which the fulminate is mixed with chlorate of potash, and sometimes also sulphide of antimony together with a small quantity of glass to increase the friction and make the cap more sensitive to percussion. A small quantity of the mixture having been put into the cap or detonator, a drop of shellac dissolved in spirit is put on it, which causes it to adhere to the metal and also gives it a waterproof covering.

Nobel's detonators contain a mixture of 70 per cent. fulminate and 30 per cent. chlorate, and the fulminate is also employed in varying charges in all the Service fuses to be fired by electricity, a little graphite being sometimes mixed with it to diminish its electrical resistance.

Silver fulminate ($Ag_2C_2N_2O_2$) is made in the same way as mercuric fulminate, silver being used instead of mercury; it is, however, far more sensitive and dangerous than the mercuric salt, and is only used in small quantities for "pull" and "throw down crackers."

CHAPTER XVII.

Sulphur Compounds.

Sulphuretted hydrogen—Preparation and properties—Combustion of sulphuretted hydrogen—Use of the compound in analysis—Preparation and properties of sulphur dioxide—Action on vegetation and life—Sulphurous acid and the sulphites—Oxidation of sulphur dioxide—Sulphur trioxide—Sulphuric acid—Manufacture of oil of vitriol—Chamber crystals—Chamber acid—Concentration of sulphuric acid—Properties and composition of sulphuric acid—The sulphates.

IT has been seen (p. 238) that sulphur occurs in Nature both free and in combination, its compounds being of very great importance, as not only do most of the metals exist in their ores as sulphides but the non-metallic elements combined with sulphur give compounds of such importance as hydric sulphide and sulphuric acid.

Hydric sulphide or sulphuretted hydrogen (H_2S) was discovered by Scheele in 1777, and exists free in Nature in the gases evolved from volcanoes, in certain mineral waters, such as those of Harrogate, and is formed when organic substances containing sulphur undergo putrefactive decay, hence its presence in sewer gas, stale eggs, &c.

Sulphuretted hydrogen can be made by the direct combination of its constituents, as when hydrogen gas is passed over or through boiling sulphur this gas is produced; the method usually employed for its preparation, however, consists of decomposing a metallic sulphide with an acid.

When ferrous sulphide (made by fusing together sulphur and iron) is acted upon by dilute sulphuric or hydrochloric acid the gas is evolved in abundance with formation of a sulphate or chloride of the metal, the action taking place in the cold :—

Ferrous sulphide		Sulphuric acid		Ferrous sulphate		Hydric sulphide.
FeS	+	H_2SO_4	=	$FeSO_4$	+	H_2S,

and this method is usually adopted in making the gas for laboratory use ; but when it is desired to carefully control its evolution, it can be obtained from antimonious sulphide and hydrochloric acid—a reaction which requires heat, and is therefore capable of being regulated :—

Antimonious sulphide		Hydrochloric acid		Antimonious chloride		Hydric sulphide.
Sb_2S_3	+	$6(HCl)$	=	$2(SbCl_3)$	+	$3(H_2S)$.

Sulphuretted hydrogen is a colourless gas, having a sweet taste and the odour of rotten eggs, and when present in the air in any quantity is very poisonous. Under a pressure of 17 atmospheres, or at − 74° C., it may be condensed to a colourless liquid which freezes at − 86° C. The gas can be decomposed by heat and is freely soluble in water, which dissolves 4.37 times its bulk of the gas at 0° C. It has a feeble acid reaction, and burns in oxygen or air. If the supply of oxygen is abundant, the sulphuretted hydrogen burns forming water and sulphur dioxide :—

Sulphuretted hydrogen		Air		Water		Sulphur dioxide		Nitrogen.
H_2S	+	$3(N_4+O)$	=	H_2O	+	SO_2	+	$6N_2$.

If, however, the supply of air is small and the quantity of oxygen therefore limited, the hydrogen burns forming water and sulphur is deposited.

The gas is decomposed by chlorine, bromine or iodine with deposition of sulphur—

Sulphuretted hydrogen		Chlorine		Hydrochloric acid		Sulphur.
$2(H_2S)$	+	$2(Cl_2)$	=	$4(HCl)$	+	S_2,

and it is also decomposed by nitric and sulphurous acids.

The tarnishing of silver in the air of towns is due to the traces of sulphuretted hydrogen present, for which silver has a great affinity; it combines with it, forming black sulphide of silver.

The action of sulphuretted hydrogen on solutions of metallic salts is of great value in analysis, and it is for this purpose that the gas is chiefly used, and by its aid the metals are separated into three main groups:—1. Metals the sulphides of which are insoluble in dilute hydrochloric acid; 2. Metals which form sulphides soluble in dilute hydrochloric acid, but insoluble in neutral or alkaline solutions; and 3. Metals which form sulphides soluble in water.

The composition of sulphuretted hydrogen can be ascertained by heating metallic tin in a known volume of the gas, when the tin combines with the sulphur forming a solid sulphide, whilst the liberated hydrogen occupies the same volume as the gas taken—

$$\overset{\text{Sulphuretted hydrogen, 2 vols.}}{SH_2} + \overset{\text{Tin}}{Sn} = \overset{\text{Stannous sulphide}}{SnS} + \overset{\text{Hydrogen, 2 vols.}}{H_2};$$

therefore like steam, sulphuretted hydrogen contains its own volume of hydrogen.

The molecular weight of the gas is 34 and its density 17. An aqueous solution of sulphuretted hydrogen has the same properties as the gas itself, and in many cases is a very convenient solution for use in analysis, but it must be remembered that a solution of the gas rapidly oxidises, the oxygen originally dissolved in the water, and absorbed from the air combining with the hydrogen, whilst sulphur is precipitated.

Sulphuretted hydrogen can at once be detected by its fœtid odour, and by its turning a piece of paper moistened with acetate of lead solution, black, owing to the formation of black sulphide of lead.

THE OXIDES OF SULPHUR.—Sulphur combines with oxygen in two proportions to form sulphur dioxide (SO_2) and sulphur trioxide (SO_3).

Sulphur dioxide, sulphurous anhydride, or sulphurous acid as it is sometimes called, has been known from the earliest times, Homer and Pliny mentioning the irritating nature of the fumes given off by burning sulphur, whilst its properties were investigated by Stahl and by Priestly in 1774, the latter demonstrating its true composition by the combustion of sulphur in oxygen. Like sulphuretted hydrogen it is found free in the gases issuing from volcanoes, and is always formed when sulphur or sulphur compounds are burnt in air or oxygen :—

$$\begin{array}{ccccc} \text{Sulphur} & & \text{Oxygen} & & \text{Sulphur dioxide.} \\ S & + & O_2 & = & SO_2. \end{array}$$

When the gas is required pure, it is prepared by heating a metal such as mercury or copper with strong sulphuric acid, when :—

$$\begin{array}{ccccccccc} \text{Copper} & & \text{Sulphuric acid} & & \text{Cupric sulphate} & & \text{Sulphur dioxide} & & \text{Water.} \\ Cu & + & 2(H_2SO_4) & = & CuSO_4 & + & SO_2 & + & 2(H_2O). \end{array}$$

In the same way when strong sulphuric acid is heated with carbon or organic matter, sulphur dioxide is evolved, but in this case carbon dioxide is formed at the same time.

$$\begin{array}{ccccccccc} \text{Carbon} & & \text{Sulphuric acid} & & \text{Carbon dioxide} & & \text{Sulphur dioxide} & & \text{Water.} \\ C & + & 2(H_2SO_4) & = & CO_2 & + & 2(SO_2) & + & 2(H_2O). \end{array}$$

It is a colourless gas, having a strong, pungent odour and an acid taste and reaction; it is freely soluble in water and in alcohol, and can be reduced to a liquid by a pressure of three atmospheres, or by a temperature of -18° C. and can be solidified at -76° C.

Nearly all classes of coals contain small traces of sulphur, which, during combustion is converted into sulphur dioxide and escapes into the air, and when present in even small traces, acts most injuriously upon vegetable life, 1 part in

10,000 of air being fatal to plants, whilst 4 parts in 10,000 render air irrespirable. Liquid sulphur dioxide will dissolve phosphorus, sulphur and iodine.

The gas does not burn or support combustion; indeed, its power of extinguishing fire has led to its use in several of the so called "grenades" and "fire extinguishers," and a handful of sulphur thrown on the fire in the grate is one of the oldest and best known remedies for a chimney on fire.

Moist sulphur dioxide has a strongly acid reaction and its solution in water may be looked upon as sulphurous acid (H_2SO_3), as although this compound has not been isolated, yet when the solution is acted upon by bases, hydrogen is replaced by the metal of the base and the class of salts called sulphites is obtained.

$$\underset{\text{Sulphurous acid}}{H_2SO_3} + \underset{\text{Sodic oxide}}{Na_2O} = \underset{\text{Sodic sulphite}}{Na_2SO_3} + \underset{\text{Water.}}{H_2O.}$$

Sulphurous acid when left exposed to air gradually takes up oxygen and becomes sulphuric acid (H_2SO_4), and this tendency to undergo oxidation renders sulphurous acid a powerful reducing agent. It is also a powerful bleaching agent, but does not so completely destroy the colouring matter as in the case of bleaching by chlorine, for the colour may in many cases be restored by acting upon the substance with a stronger acid or an alkali. It is largely used for bleaching straw, wool and silk, and is also employed as a deodoriser and as an antiseptic to prevent fermentation and decay. It has a molecular weight of 64 and a density of 32.

Under ordinary conditions sulphur dioxide will not directly combine with more oxygen, but if a mixture of sulphur dioxide and oxygen be passed over heated platinum or platinised asbestos, the strong surface action exercised by the platinum causes combination to take place and dense white fumes of sulphur trioxide (SO_3) are formed. The trioxide is more conveniently prepared by warming Nordhausen sulphuric acid, a fuming acid made by distilling ferrous sulphate and which consists of sulphur trioxide dissolved in sulphuric acid. Under the influence of heat the sulphur trioxide is driven off and may be condensed in a cooled receiver.

$$\underset{\text{Nordhausen acid}}{H_2S_2O_7} = \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Sulphur trioxide.}}{SO_3.}$$

Sulphur trioxide is a white silky crystalline body, having a specific gravity of 1.95 and melting at temperatures varying between 15° C. and 32° C., according to its crystalline condition; when exposed to air it yields dense white fumes and absorbing moisture rapidly becomes liquid. At a high temperature it is decomposed into oxygen and sulphur dioxide. When free from moisture it is not acid to dry litmus, but becomes acid immediately on absorbing moisture; on bringing it in contact with water it combines with it with great energy, giving off great heat and hissing as if red hot iron had been plunged into the water, instantly forming sulphuric acid (H_2SO_4).

$$\underset{\text{Sulphur trioxide}}{SO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4.}$$

Sulphuric acid, hydric sulphate or oil of vitriol (H_2SO_4) is the most important of the acids.

It is used to an enormous extent in the arts and manufactures; indeed so many industries are dependent upon it that Liebig has said with considerable truth that "the civilisation of a country may be roughly gauged by the amount of sulphuric acid manufactured in it."

The present method of manufacturing sulphuric acid may be said to date from 1786, where Dr. Roebuck made the acid by burning sulphur with saltpetre in leaden vessels and condensing the fumes in water.

The principle of the method at present employed is the same as that of Roebuck's process, and is that whilst sulphur dioxide is not able even in presence of water to rapidly absorb oxygen from the air, it can readily take it from some of the oxides of nitrogen, which, in turn can again take oxygen from the air, and may in this way be made the medium for rapidly oxidising sulphur dioxide in the presence of water with formation of sulphuric acid. The manufacture of sulphuric acid as at present carried out consists in burning sulphur or iron pyrites in a current of air in the furnace (A, Fig. 51) and leading the mixture of nitrogen, oxygen and sulphur dioxide so produced over a vessel (B) containing some sodic nitrate, and sulphuric acid, which, becoming heated by the gases evolves vapours of nitric acid.

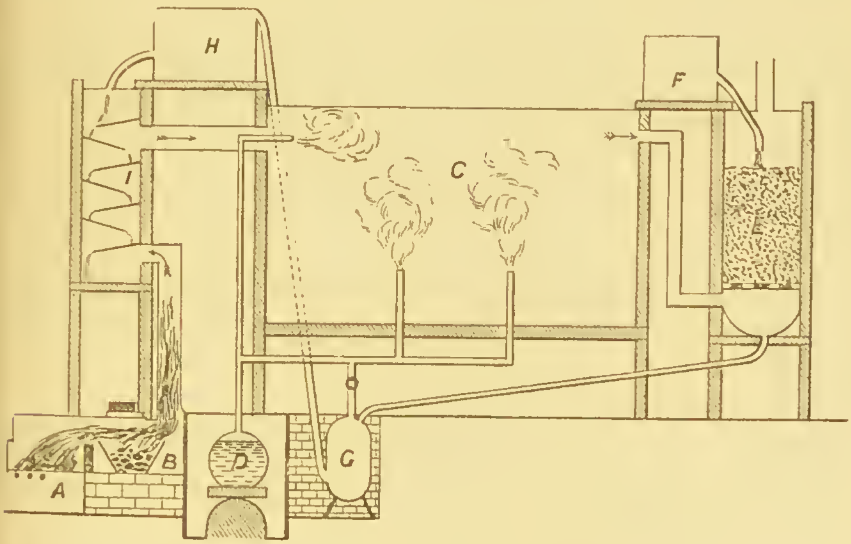

Fig. 51.

Sodic nitrate		Sulphuric acid		Sodic bisulphate		Nitric acid.
$NaNO_3$	$+$	H_2SO_4	$=$	$NaHSO_4$	$+$	HNO_3.

The nitric acid passes on with the mixed gases into large leaden chambers, one of which is shown at (C, Fig. 51), and is attacked and reduced by the sulphur dioxide, with the formation of nitrogen trioxide and sulphuric acid in the presence of water vapour.

$$\overset{\text{Sulphur dioxide}}{2(SO_2)} + \overset{\text{Nitric acid}}{2(HNO_3)} + \overset{\text{Water}}{H_2O} = \overset{\text{Sulphuric acid}}{2(H_2SO_4)} + \overset{\text{Nitrogen trioxide.}}{N_2O_3}.$$

The nitrogen trioxide so formed, in contact with more sulphur dioxide, oxygen from the air, and water vapour, forms a white crystalline compound known by the name of "Chamber crystals."

$$\overset{\text{Nitrogen trioxide}}{N_2O_3} + \overset{\text{Oxygen}}{O_2} + \overset{\text{Sulphur dioxide}}{2(SO_2)} + \overset{\text{Water}}{H_2O} = \overset{\text{Chamber crystals.}}{2(HSO_3NO_2)},$$

and steam being blown into the leaden chambers from the boiler (D), these crystals dissolve with formation of sulphuric acid and elimination of the nitrogen trioxide.

$$\overset{\text{Chamber crystals}}{2(HSO_3NO_2)} + \overset{\text{Water}}{H_2O} = \overset{\text{Sulphuric acid}}{2(H_2SO_4)} + \overset{\text{Nitrogen trioxide.}}{N_2O_3}.$$

The nitrogen trioxide, however, can still give up another atom of oxygen to sulphur dioxide and water, forming nitrogen dioxide:—

$$\overset{\text{Nitrogen trioxide}}{N_2O_3} + \overset{\text{Water.}}{H_2O} + \overset{\text{Sulphur dioxide}}{SO_2} = \overset{\text{Sulphuric acid}}{H_2SO_4} + \overset{\text{Nitrogen dioxide.}}{2(NO)}$$

and the further course of the reactions in the acid chambers may be looked upon as a continual taking up of oxygen from the air by the nitrogen dioxide, and reduction of the nitrogen trioxide formed, by the sulphur dioxide and water, with formation of sulphuric acid and liberation of nitrogen dioxide, which is again ready to perform its function as a carrier of oxygen from the air to the sulphur dioxide and water. The water needed in the reaction is either blown into the chambers in a fine spray or as steam, and condensing, carries down the sulphuric acid to the floor of the chambers.

It is evident that, theoretically, the small amount of oxides of nitrogen first introduced should be able to convert an unlimited amount of sulphur dioxide into sulphuric acid, but in order to supply the oxygen necessary to the reaction, very large quantities of air must be drawn into the chambers, and the residual nitrogen must be removed, and the constant removal of the nitrogen from the chambers carries away a large percentage of the nitrous fumes, and necessitates their constant renewal. The escaping gases from the chambers are made to pass up a brick shaft filled with flints and called the "Glover's tower" (E, Fig. 51), down which a mixture of strong nitrated sulphuric acid and chamber acid (the weak sulphuric acid from the chambers) is allowed to flow from a cistern (F), and meets the escaping gases from the chamber; the sulphuric acid absorbs the nitrous fumes, and forms a compound called nitro-sulphuric acid, which is collected in (G), and from which the oxides of nitrogen can be again recovered and sent back into the chambers, by making the hot gases pass through thin streams of it in shaft (I).

The acid formed in the chambers is not allowed to attain a higher specific gravity than 1.55, as above this point of concentration it would absorb the nitrous fumes. It is run into leaden evaporating pans, and flame and hot air are allowed to play over the surface of the acid, water being evaporated and the specific gravity of the acid raised to 1.71, beyond which it is impossible to concentrate it in leaden vessels, as the hot acid would attack the lead. This strength of acid is sold for many manufacturing purposes and is technically known as B.O.V. (brown oil of vitriol), the colour being due to the presence of small quantities of carbonised organic matter.

Further concentration is effected in glass or platinum stills, until dense fumes of sulphur trioxide begin to escape, when the acid is drawn off and has now a density of 1.84.

The concentrated sulphuric acid is a heavy, oily liquid. having no smell and an intensely corrosive action; it boils at 388° C., and at this temperature gives off clouds o white fumes; it has a great affinity for water and when mixed with it evolves great heat and combines forming definite hydrates. If left exposed to air it rapidly increases in volume from the absorption of water vapour from the air and this property makes it valuable as a dessicating (drying) agent, as substances containing moisture can be placed over a pan or dish of the acid under an air-tight glass shade, the acid drying the air in the confined space and so promoting evaporation from the substance to be dried. Similarly, gases which are not acted upon by the acid can be effectually dried by passing them through tubes containing (ignited) pumice stone saturated with the strongest acid, a large surface thus being presented to the passing gases. This affinity for water is also shown in the action of the strong acid on substances of organic origin, containing besides carbon, oxygen and hydrogen in the proportions necessary to form water, when the combination of the hydrogen and oxygen is determined by the presence of the acid and in many cases the carbon is liberated. The action is well illustrated by pouring an equal volume of the strongest sulphuric acid into a saturated sugar syrup, when the sugar is decomposed, the hydrogen and oxygen extracted as water by the acid and a spongy mass of carbon occupying many times the bulk of the original liquid is obtained.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{Sulphuric acid}}{xH_2SO_4} = \underset{\text{Dilute acid}}{xH_2SO_4,11(H_2O)} + \underset{\text{Carbon.}}{12C.}$$

Even when very dilute, sulphuric acid has a powerful "rotting" action on all textile fabrics, for if too dilute to do much damage at first, it gradually becomes more concentrated by evaporation of the water and attacks the fibre. Dropped upon black or dark coloured fabrics, sulphuric acid gives a red stain, which, however, can be removed by neutralising the acid with ammonia, and then sponging with a little water to remove the salt formed. Hydrochloric acid stains can be removed in the same way, but nitric acid gives a yellow stain which cannot be got rid of.

At a red heat the vapour of sulphuric acid is decomposed into steam, sulphur dioxide and oxygen, and this has been proposed as a method for the preparation of oxygen, as it can readily be freed from the sulphur dioxide by washing with an alkaline solution.

With the exception of gold and platinum all the metals are acted upon by boiling concentrated sulphuric acid, a sulphate of the metal being formed and sulphur dioxide liberated.

Mercury		Sulphuric acid		Mercuric sulphate		Sulphur dioxide		Water.
Hg	$+$	$2(H_2SO_4)$	$=$	$HgSO_4$	$+$	SO_2	$+$	$2(H_2O)$.

When unsized paper is soaked in a cold mixture of two volumes of concentrated sulphuric acid and one volume of water, it is converted into a substance called "vegetable parchment," which must be freed from acid by well washing with water; it is a tough translucent substance much used for covering jam pots, and other purposes, for which animal parchment was at one time employed.

The large and important class of salts called sulphates consists of the acid radicle (SO_4) in combination with metals, and inasmuch as on analysis, sulphuric acid is found to contain its constituents in the proportion—

Hydrogen	2
Sulphur	32
Oxygen	64

and as the hydrogen can be replaced in two stages by a monad metal forming two classes of salts corresponding to the formulæ:—

$NaHSO_4$ (Sodic bisulphate),
Na_2SO_4 (Sodic sulphate),

it is evident that the formula for sulphuric acid will be H_2SO_4.

When 98 parts by weight of sulphuric acid are converted into vapour, the vapour is found to occupy four volumes instead of two, but this is due to the dissociation (temporary decomposition) of the molecule into water vapour and sulphur trioxide.

Sulphuric acid		Water vapour		Sulphur trioxide.
H_2SO_4	$=$	H_2O	$+$	SO_3
2 vols.		2 vols.		2 vols.

Sulphuric acid and its salts when in solution may be recognised by their giving a white precipitate with soluble barium salts; this precipitate is baric sulphate, which is practically insoluble in all acids.

Sulphur forms many other compounds of great scientific and industrial importance, but which do not come within the scope of the present work.

CHAPTER XVIII.

THE HALOGENS.

Chlorine—Preparation of the gas—Deacon's process—Properties of chlorine—Bleaching action dependent on moisture—Hydrochloric acid gas—Preparation and properties—Effect of hydrochloric acid gas on vegetation—Chlorides—Chlorine monoxide—Hypochlorous acid—Bleaching powder—Hypochlorites and chlorates—Potassic chlorate—Percussion caps—Friction tubes—Coloured fires—Bromine and Iodine—Preparation and properties—Bromides and iodides—Fluorine—Isolation of Fluorine—Fluor spar—Hydrofluoric acid—Etching on glass—Gradations of chemical and physical properties in the halogens.

CHLORINE gas was discovered in 1774 by Scheele, and its elementary character was proved by Thénard and Davy in 1809–1810.

It is never found free in Nature, but abundantly in combination with sodium and other metals, and is found in all animal secretions.

The gas is most easily prepared by heating together a mixture of black oxide of manganese (the mineral pyrolusite) and strong hydrochloric acid, the reaction taking place in two stages—

$$\overset{\text{Pyrolusite}}{MnO_2} + \overset{\text{Hydrochloric acid}}{4(HCl)} = \overset{\text{Manganese tetrachloride}}{MnCl_4} + \overset{\text{Water,}}{2(H_2O),}$$

and manganic tetrachloride only existing at low temperatures, breaks up on warming into manganous chloride and chlorine gas.

$$\overset{\text{Manganic tetrachloride}}{MnCl_4} = \overset{\text{Manganous chloride}}{MnCl_2} + \overset{\text{Chlorine.}}{Cl_2.}$$

This is the method by which Scheele first prepared chlorine, and it is still employed as the most convenient laboratory method of making the gas. When used on a manufacturing scale the manganous chloride is again converted into the black oxide by treating with lime, which forms calcic chloride and manganese oxide (MnO), the latter being oxidised to the black oxide (MnO_2) by mixing with more lime and blowing air through the mixture (Weldon's process).

It can be prepared from common salt by mixing the salt (sodic chloride) with pyrolusite and sulphuric acid and warming the mixture :—

$$\overset{\text{Sodic chloride}}{2(NaCl)} + \overset{\text{Pyrolusite}}{MnO_2} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$

$$= \overset{\text{Sodic sulphate}}{Na_2SO_4} + \overset{\text{Manganous sulphate}}{MnSO_4} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Chlorine.}}{Cl_2}.$$

Whilst on a manufacturing scale it is now largely prepared by "Deacon's process." A mixture of air and hydrochloric acid gas is passed over heated firebricks saturated with sulphate or chloride of copper, when the alternate formation and decomposition of cupric chloride gives chlorine gas. The final action may be represented as :

$$\overset{\text{Hydrochloric acid}}{2(HCl)} + \overset{\text{Air}}{(N_4+O)} = \overset{\text{Water}}{H_2O} + \overset{\text{Nitrogen}}{2N_2} + \overset{\text{Chlorine.}}{Cl_2}.$$

The chlorine obtained is mixed with twice its volume of nitrogen, but for the processes in which it is employed this does not matter.

Chlorine is a yellowish green gas which is volume for volume 35.5 times heavier than hydrogen ; it has an insupportable odour and when inhaled in even very minute traces causes great irritation of the mucous lining of the throat and lungs ; air containing 5 per cent. of it rapidly proving fatal to animals.

It can be liquefied under a pressure of 6 atmospheres at 0° C., but cannot be converted into a solid even at a temperature of −140° C. At ordinary temperatures, water dissolves a little more than 2.5 times its volume of the gas, and if the solution be cooled down to 0° C., crystals of a solid hydrate separate from the solution, their composition being ($Cl_2 10H_2O$).

Chlorine gas is not combustible in air or oxygen, and will only support the combustion of certain metals, or substances rich in hydrogen, combining with the hydrogen of the body to form hydrochloric acid whilst the carbon is deposited.

Chlorine has an intense affinity for hydrogen and the metals, a mixture of equal volumes of chlorine and hydrogen combining with explosion when subjected to direct sunlight; whilst many metals like antimony or copper in a fine state of division, spontaneously ignite when thrown into the gas, chlorides of the metals being produced. The affinity of chlorine for hydrogen, makes chlorine a very powerful oxidising agent, as when it comes in contact with any moist substance which can be readily oxidised, the chlorine combines with the hydrogen of the moisture, forming hydrochloric acid whilst the nascent oxygen combines with the oxidisable substance.

This explains why it is that moist chlorine will bleach many colouring matters, whilst the dry gas has no effect upon them; the bleaching action of chlorine being an oxidation at the expense of the oxygen of the water present. Colours bleached by chlorine are destroyed, and cannot, as in the case of bleaching by sulphur dioxide, be restored.

When a solution of chlorine in water is exposed to daylight it rapidly loses its characteristic yellow colour and becomes colourless, oxygen being at the same time liberated, an action due to the chlorine under the influence of light decomposing the water:—

$$\overset{\text{Water}}{2(H_2O)} + \overset{\text{Chlorine}}{2Cl_2} = \overset{\text{Hydrochloric acid}}{4(HCl)} + \overset{\text{Oxygen.}}{O_2}.$$

Chlorine does not combine directly with either carbon or oxygen; phosphorus catches fire spontaneously in it, forming chiefly phosphorus trichloride (PCl_3), and sulphur will burn feebly in it; whilst selenium, boron and silicon will combine with it when heated.

The great affinity for hydrogen displayed by chlorine renders its action on organic compounds very powerful: in some cases spontaneous combustion taking place as when, blotting paper moistened with fresh turpentine is plunged into the gas.

When hydrogen or substances containing hydrogen are burnt in chlorine gas, hydrochloric acid gas is formed, and consists, as has been shown (p. 35), of a combination of equal volumes of the two elements, the hydrochloric acid gas occupying the same volume as was occupied by the hydrogen and chlorine forming it.

So great is the affinity of the two elements for each other, that if they are mixed in equal volumes, and exposed to any light rich in the chemically active rays which are found at the violet end of the spectrum, such as direct sunlight, the light from burning magnesium, or the flash obtained by igniting a mixture of carbon disulphide vapour and nitrogen dioxide, the two gases combine with explosion, whilst even in diffused daylight they gradually combine without explosion, in each case forming their own volume of hydrochloric acid gas. A mixture of the two gases however, may be kept for an indefinite period in the dark, but will combine when brought into the light, or under the influence of heat or an electric spark.

Hydrochloric acid is found in volcanic gases, and also occasionally in the spring waters of volcanic districts, whilst its salts are amongst the most important natural compounds.

For laboratory use it is always prepared by acting upon salt with sulphuric acid, when—

$$\overset{\text{Sodic chloride}}{\mathrm{NaCl}} + \overset{\text{Sulphuric acid}}{\mathrm{H_2SO_4}} = \overset{\text{Sodic bisulphate}}{\mathrm{NaHSO_4}} + \overset{\text{Hydrochloric acid gas.}}{\mathrm{HCl}},$$

an interchange taking place between the sodium and one atom of hydrogen of the sulphuric acid, with formation of hydrochloric acid gas and sodic bisulphate.

In preparing the gas in this way it is found convenient to fuse the salt before using it, in order to reduce the surface exposed and thus prevent the excessive frothing which attends the use of ordinary table salt.

At temperatures which can be safely employed in a glass flask the above reaction takes place, but at a higher temperature, such as is attained in the salt cake furnace of the soda manufacturer, both atoms of hydrogen in the sulphuric acid can be replaced by sodium and double the volume of hydrochloric acid gas is obtained :—

$$\overset{\text{Sodic chloride}}{2(\mathrm{NaCl})} + \overset{\text{Sulphuric acid}}{\mathrm{H_2SO_4}} = \overset{\text{Sodic sulphate}}{\mathrm{Na_2SO_4}} + \overset{\text{Hydrochloric acid.}}{2(\mathrm{HCl})}.$$

The gas so obtained must be collected over mercury or by downward displacement of air, as it is so intensely soluble in water that it would be impossible to utilise it for its collection. The experimental data by which the composition of the gas has been proved have been fully given (p. 35). The molecular weight of the gas is 36.5 and its density 18.25. It is a transparent, colourless gas with a suffocating odour and acid taste; it forms dense fumes on escaping into the air. These fumes are due to the gas attracting moisture from the air and condensing it.

Hydrochloric acid gas can be condensed to a liquid by a pressure of 40 atmospheres and the anhydrous liquid has few of the properties of the solution of the gas in water; it has little or no action upon the metals, it hardly affects dry litmus and has no action upon calcic carbonate or quicklime.

When this gas is present in the air in even small traces (1 in 25,000) it has a most destructive effect upon vegetation, causing the leaves to quickly wither and shrivel up, an effect which is supposed to be due to the attraction which the acid gas has for moisture. The effect of traces of this gas in the air may be seen in the pottery districts, where large areas are practically denuded of vegetation by the hydrochloric acid evolved during the process of salt glazing.

The liquid hydrochloric acid of commerce, called muriatic acid, or spirits of salt, is a solution of the gas in water. One pint of water at ordinary temperature will absorb nearly 500 pints of hydrochloric acid gas, forming 1⅓ pint of the solution, having a specific gravity of 1.21.

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid as a preliminary step in the manufacture of sodic carbonate, and the alkali maker is compelled by Act of Parliament to condense the hydrochloric acid gas evolved, as otherwise it would escape into the air, and wither up all the vegetation in the neighbourhood. The gas is condensed by making it pass up a flue containing lumps of coke, over which water is slowly trickling down; the water dissolves the hydrochloric acid gas, and the solution is drawn off at the bottom of the flue.

Pure hydrochloric acid solution is colourless, but the crude acid nearly always has a yellow colour, due to the presence of iron.

If the strongest acid, having a specific gravity of 1.21 is cooled down to—18° C., it deposits crystals having the composition $HCl,4(H_2O)$.

Most of the metals with the exception of gold and platinum are acted upon by hydrochloric acid, forming a chloride of the metal, which is also obtained when a metallic oxide is acted on by the acid. The molecule of hydrochloric acid only containing one atom of hydrogen, no acid chlorides can be formed.

Chlorides in solution can be detected by their forming a white precipitate with soluble silver salts, which is insoluble in nitric acid but soluble in ammonia, whilst all chlorides when heated with peroxide of manganese and sulphuric acid, evolve chlorine.

In its great affinity for the metals, chlorine resembles oxygen, and as a rule, the more closely elements resemble each other the less will be their affinity for each other, and chlorine cannot be made to directly combine with oxygen although by indirect processes it forms several oxides.

If dry chlorine gas be passed over dry precipitated mercuric oxide, a substance called chlorine monoxide passes off and may be condensed as a red liquid in a tube surrounded with ice and salt.

$$\overset{\text{Mercuric oxide}}{2(HgO)} + \overset{\text{Chlorine}}{2Cl_2} = \overset{\text{Mercuric oxychloride}}{HgO,HgCl_2} + \overset{\text{Chlorine monoxide.}}{Cl_2O.}$$

This liquid boils at +19° C., and any elevation of temperature causes it to explode; it is rapidly absorbed by water, and the solution is supposed to contain hypochlorous acid, which however, has not been isolated, although its salts are well known in an impure condition.

$$\overset{\text{Chlorine monoxide}}{Cl_2O} + \overset{\text{Water}}{H_2O} = \overset{\text{Hypochlorous acid.}}{2(HClO).}$$

The most important compound formed by this acid is calcic hypochlorite, which in its crude state is known as "Bleaching Powder"—the chloride of lime of the oilshops. This is made by taking freshly burnt quicklime, free from iron, and slaking it, sifting to remove lumps, and spreading it in thin layers on stone shelves fitted in a stone, brick, or sometimes lead chamber, the shelves being so arranged that they are open alternately back and front, so that gas passing through the chamber traverses the surface of each shelf; small openings with glass doors are made in the side of the chamber, so that the operation can be watched and the lime raked over once or twice during its conversion into bleaching powder. Chlorine gas is now generated in a stone "still," and the gas is made to pass over the slaked lime, care being taken to keep the temperature as low as possible, as the heat, which would be developed if the absorption went on too rapidly, would reduce the strength of the bleaching powder owing to the formation of calcic chlorate instead of calcic hypochlorite. The operation is continued for about 36 hours, by which time it is complete, and the bleaching powder contains from 30 to 39 per cent. of chlorine which can be rendered available for bleaching purposes.

Bleaching powder depends for its action upon the calcic hypochlorite which it contains, but is itself a complex substance, probably having the composition—

$$\underset{\text{Bleaching powder.}}{Ca_3(HO)_2(ClO)_2Cl_2.}$$

Its formation being represented by the equation—

$$\underset{\text{Slaked lime}}{3\Big(Ca(HO)_2\Big)} + \underset{\text{Chlorine}}{2Cl_2} = \underset{\text{Bleaching powder}}{Ca_3(HO)_2(ClO)_2Cl_2} + \underset{\text{Water.}}{2(H_2O).}$$

It is probably a feeble compound of this composition, as if it were a mixture of calcic hydrate, hypochlorite and chloride, the latter salt would make it highly deliquescent, which is not the case with good bleaching powder.

The bleaching action of the compound is due to the fact that bleaching powder gives off chlorine gas when it comes in contact with any acid, even carbonic acid being strong enough to liberate it.

$$\overset{\text{Bleaching powder}}{Ca_3(HO)_2(ClO)_2Cl_2} + \overset{\text{Carbon dioxide}}{3(CO_2)} = \overset{\text{Calcic carbonate}}{3(CaCO_3)}$$

$$+ \overset{\text{Water}}{H_2O} + \overset{\text{Chlorine.}}{2Cl_2}.$$

In using it on a large scale a solution of the bleaching powder in water is taken, and the fabrics to be bleached are dipped into it, and after being allowed to soak for some hours are then transferred for a short time to a tank containing very dilute acid, by which the chlorine is liberated in the material itself. When the bleaching is completed, which may require two or three dippings, the articles are well washed and boiled in a dilute solution of sodic carbonate, to remove the colouring matter rendered soluble by the chlorine, and to get rid of all traces of free acid, which, if allowed to remain, would render the fabric rotten.

Chloride of lime is of value as a disinfectant, breaking up moisture, and thus oxidising and destroying organic germs; it also decomposes noxious gases, like sulphuretted hydrogen, taking the hydrogen to form hydric chloride and depositing the sulphur.

If chlorine gas is passed into dilute cold solution of potassic hydrate, the chlorine is absorbed, and chloride and hypochlorite of potassium formed in the solution which is technically known as "Eau de Javelles" and which was the first artificial bleaching agent used:—

$$\overset{\substack{\text{Potassic}\\ \text{hydrate}}}{2(KHO)} + \overset{\text{Chlorine}}{Cl_2} = \overset{\substack{\text{Potassic}\\ \text{chloride}}}{KCl} + \overset{\substack{\text{Potassic}\\ \text{hypochlorite}}}{KClO} + \overset{\text{Water.}}{H_2O},$$

and if this solution be boiled, the hypochlorite breaks up into potassic chloride and chlorate:—

$$\underset{\text{Potassic hypochlorite}}{3(KClO)} = \underset{\text{Potassic chloride}}{2(KCl)} + \underset{\text{Potassic chlorate.}}{KClO_3}.$$

Potassic chlorate may be formed in one operation, by passing chlorine into a hot strong solution of potassic hydrate :—

$$\underset{\text{Potassic hydrate}}{6(KHO)} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Potassic chloride}}{5(KCl)} + \underset{\text{Potassic chlorate}}{KClO_3} + \underset{\text{Water.}}{3(H_2O)};$$

and if this solution be concentrated and allowed to stand, the potassic chloride which is soluble in three times its weight of cold water remains in solution, whilst the chlorate requiring 16 times its weight of cold water to dissolve it, separates out in tabular crystals.

On a manufacturing scale a paste of potassic carbonate and slaked lime is saturated with chlorine, and treated with boiling water, which dissolves out the calcic chloride and potassic chlorate formed, and the former salt being very soluble in water, the chlorate is easily separated by crystallisation.

Potassic chlorate ($KClO_3$) is formed from an acid called chloric acid ($HClO_3$) by replacing the atom of hydrogen by potassium, and in the same way the class of salts called chlorates may all be built up.

The chlorates, like the nitrates, are all strong oxidising agents acting, however, at lower temperatures, because they part with their oxygen more easily; the oxidation by potassic chlorate is also much more violent than the action of the nitrate, as the chlorate is one of the few compounds which give out heat during decomposition instead of absorbing it, and for this reason potassic chlorate is called an "endothermic" compound, and this property enhances the rapidity and vigour with which the salt acts.

A unit weight of potassic chlorate evolves during decomposition enough heat to raise 39 unit weights of water 1° C., hence we say it gives out 39 thermal units. At high temperatures potassic chlorate acts violently upon combustible bodies, and it has been already seen that it is the source from which oxygen gas is obtained.

A few grains of sulphur mixed with potassic chlorate and rubbed in a mortar detonate violently, and before the introduction of mercuric fulminate this mixture was used for percussion caps, for which, however, it was ill adapted as it caused serious corrosion of the nipple of the gun.

A mixture of antimony sulphide and potassic chlorate will detonate when struck with a hammer, and is used in friction tubes for firing cannon. Friction tubes consist of a quill tube filled with powder, in the upper part of which a small rasp surrounded by the mixture is fixed, and on rapidly pulling this out by means of a cord the friction fires the mixture which in turn ignites the powder. For military use the tube is of copper.

Potassic chlorate has been employed as an ingredient of explosives, but many compositions in which it plays a part are liable to spontaneous combustion, added to which its effects are so uncertain and violent that it is rarely licensed as an explosive in England,* although used abroad; it however plays an important part in nearly all coloured fires, port lights, etc., the compositions of some of which are given below, the colour being imparted by various metallic salts :—

Red fire—

Potassic chlorate	6.0	parts by weight.
Strontic nitrate	40.0	,, ,,
Sulphur	13.0	,, ,,
Carbon	2.0	,, ,,

Green fire—

Potassic chlorate	32.7	parts by weight.
Baric nitrate	52.3	,, ,,
Sulphur	9.8	,, ,,
Carbon	5.2	,, ,,

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* "Asphaline" is at present the only chlorate explosive licensed in this country.

White fire—

Potassic chlorate	48.0	parts by weight.	
Sulphur	13.25	,,	,,
Antimony Sulphide	7.25	,,	,,

Blue fire—

Potassic chlorate	36.0	parts by weight.	
Cupric chloride	24.0	,,	,,
Mercuric chloride	1.0	,,	,,
Sulphur	14.0	,,	,,

The elements bromine and iodine so strongly resemble chlorine in all their properties that the three are classed together with fluorine, these elements being commonly called "the halogens" or salt producers, from the fact that when an atom of one of them exists in combination with an atom of potassium or sodium, the compound strongly resembles sodic chloride or common salt in properties.

The principal source of sodic chloride is sea water, and the salts of bromine and iodine are also chiefly obtained from it.

Bromine was discovered in 1826, by Balard, who obtained it from the solution left after concentrating sea water and crystallising out the sodic chloride, and at first, supposed it to be a compound of iodine and chlorine. Like chlorine, it never occurs free in Nature and its salts are found in company with the chlorides in sea water and the waters of many mineral springs.

When crude sodic chloride, known as "bay salt," has been crystallised out from sea water after evaporation, the mother liquor or "bittern" contains magnesic and sodic bromide and from this source the bromine is generally obtained. Bromine is first liberated by addition of chlorine water, when the chlorine having a stronger affinity for the metal than bromine, turns it out, a chloride being formed—

$$\begin{array}{ccccccc}\text{Sodic bromide} & & \text{Chlorine} & & \text{Sodic chloride} & & \text{Bromine.} \\ 2(NaBr) & + & Cl_2 & = & 2(NaCl) & + & Br_2.\end{array}$$

This mixture is then agitated with ether in which the bromine is more soluble than in water; the ether extracts the bromine from its aqueous solution and rises to the surface, forming a layer, which can be easily drawn off.

The ethereal solution now has potassic hydrate added to it and is heated, when the ether distils off and is condensed for further use, while the bromine is left behind as bromide and bromate.

$$\overset{\text{Bromine}}{3Br_2} + \overset{\text{Potassic hydrate}}{6(KHO)} = \overset{\text{Potassic bromide}}{5(KBr)} + \overset{\text{Potassic bromate}}{KBrO_3} + \overset{\text{Water.}}{3(H_2O)}.$$

This residue is now heated to a fairly high temperature, which decomposes the bromate, bromide being formed:

$$\overset{\text{Potassic bromate}}{2(KBrO_3)} = \overset{\text{Potassic bromide}}{2(KBr)} + \overset{\text{Oxygen.}}{3O_2},$$

and the potassic bromide is now mixed with peroxide of manganese and sulphuric acid, and the mixture distilled, bromine escaping free as an orange red vapour which is condensed by cooling to a dark reddish brown liquid, which evolves red brown vapour at ordinary temperatures.

$$\overset{\text{Potassic bromide}}{2(KBr)} + \overset{\text{Peroxide manganese}}{MnO_2} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$

$$= \overset{\text{Manganous sulphate}}{MnSO_4} + \overset{\text{Potassic sulphate}}{K_2SO_4} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Bromine.}}{Br_2}.$$

Bromine and mercury are the only two elements liquid at ordinary temperatures.

The vapour has an excessively corrosive and irritating smell and acid taste and is an active poison. Volume for volume bromine vapour is 80 times as heavy as hydrogen. Liquid bromine boils at 63° C. and solidifies at – 20° C., and is soluble in water, 34 parts of water dissolving one of bromine.

The vapour of bromine like chlorine only supports the combustion of substances rich in hydrogen, and it also bleaches certain colours by oxidation in the presence of moisture.

Bromine combines with hydrogen to form hydrobromic acid (HBr), but the tendency to combination is much feebler than is the case with chlorine, the mixed gases having to be passed through a red hot tube to make them combine.

Hydrobromic acid forms the class of salts called bromides, much used in medicine and photography, but for other purposes it is of but little practical use, and the same remark applies to the compounds formed by bromine and oxygen.

Iodine was discovered in 1812, by Courtois, and like bromine it occurs chiefly in sea and certain mineral spring waters. Sea water only contains about 1 part of iodine compounds in 250,000 parts of water, but seaweeds during their growth collect the traces from the sea water, and when the weeds are collected and burnt, the iodides are found in the ash. On the coast of Scotland and the neighbouring islands, enormous quantities of seaweed are collected and burnt, and the ash which is called "kelp" is then exhausted with water, and on evaporating the solution potassic sulphate crystallises out; this is removed and on further concentration and cooling a crop of crystals of potassic chloride, together with sulphate, chloride and carbonate of soda, is obtained, and the mother liquor, which contains bromides as well as iodides, is then mixed with sulphuric acid and is put into a retort, peroxide of manganese is added, and the retorts are heated and the iodine distils over as a violet vapour, which is condensed in cooled receivers as a greyish black shining solid, which crystallises in metallic looking scales.

$$\overset{\text{Potassic iodide}}{2(KI)} + \overset{\text{Peroxide of manganese}}{MnO_2.} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$

$$\overset{\text{Manganous sulphate}}{MnSO_4} + \overset{\text{Potassic sulphate}}{K_2SO_4} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Iodine.}}{I_2.}$$

When no more iodine distils over, more peroxide of manganese is added and the temperature raised when the bromine present in the liquid distils over.

The iodine so obtained is purified by resublimation and is generally found in rhomboidal plates, having a lustre like graphite. It melts at 107° C. and boils at 175° C., being converted into a magnificent violet vapour which is 127 times heavier, bulk for bulk, than hydrogen. It is but little soluble in water, 7,000 parts only dissolving one of iodine, but is readily soluble in alcohol, ether, bisulphide of carbon or the alkaline iodides. Iodine and the iodides are much used in medicine and photography, but neither the element or its compounds with hydrogen or oxygen have many practical applications.

Iodine has not so strong an affinity for hydrogen or the metals as either chlorine or bromine, both of which will turn it out of combination. Of these three elements chlorine has the strongest affinity for hydrogen and the metals and iodine the feeblest, bromine being intermediate in its affinity. This order is reversed in their combinations with oxygen, iodine being the strongest and chlorine the weakest.

The fact that iodine can be liberated from its compounds by the addition of a drop of chlorine water can be utilised as a very delicate test for the iodides. If an iodide is mixed with a dilute solution of starch no change in colour takes place, but if a drop of chlorine water be now added, the iodine will at once be liberated and blue iodide of starch will be formed, even if the quantity of iodine present, be exceedingly small.

FLUORINE.—The compounds of this element have been recognised as containing it since the close of the last century; but its affinity for nearly all other substances is so great that, in spite of the many attempts to isolate it, it remained unknown in the free state until 1887,* when it was obtained by electrolysing pure hydrofluoric acid, in which potassic hydrofluoride had been dissolved to render it a better conductor of electricity, a platinum U tube being employed, an electrode of platinum-iridium alloy being used as the positive pole, whilst the negative consisted of platinum only; the U tube was provided with stoppers of fluor spar, and platinum delivery tubes were used for the gaseous products. Under these conditions, and at a temperature of – 23° C., fluorine was obtained as a colourless gas which decomposes water, liberating oxygen and combining with the hydrogen to form hydrofluoric acid; when brought in contact with hydrogen gas it exploded, even in the dark, and combined with nearly all the elements with combustion, oxygen and carbon alone being unaffected by it.

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* Moissan.

Fluorine occurs in Nature chiefly in combination with calcium as calcic fluoride (CaF_2), which is found in enormous quantities as fluor or Derbyshire spar, which forms crystals belonging to the cubical system and is often very beautifully coloured by traces of metallic oxides.

This mineral has been used from the earliest ages as a flux in metallurgical processes, and rather more than a century ago it was discovered that when it was heated with sulphuric acid, fumes were given off which had the property of rapidly corroding glass, and these fumes were afterwards shown by Gay-Lussac and Thénard to consist of a compound containing hydrogen united with the then not yet isolated element fluorine.

This method is still that employed for its preparation and the reaction which takes place may be represented as—

$$\underset{\text{Calcic fluoride}}{CaF_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Calcic sulphate}}{CaSO_4} + \underset{\text{Hydrofluoric acid.}}{2(HF).}$$

This gas, which is called hydrofluoric acid, and which contains one part by weight of hydrogen combined with 19 parts by weight of fluorine, forms dense white fumes when in contact with air. When obtained by this method the escaping vapour can be condensed to a liquid by passing it through a tube cooled by a mixture of ice and salt, and the liquid so obtained was long considered to be liquid hydrofluoric acid, but is, in reality, a concentrated solution of hydrofluoric gas in water, the anhydrous acid being obtained from this by distilling it with phosphoric pentoxide.

When perfectly anhydrous, the gas has little or no action on glass, but in solution, or in the presence of moisture, it rapidly attacks it, dissolving out some of the silica from it and forming a compound called silicon fluoride.

Hydrofluoric acid, in many of its properties, bears a strong resemblance to hydrochloric acid, but its action upon glass and substances containing silica distinguishes it from all other compounds.

In consequence of this property, it cannot be prepared in vessels of glass or porcelain, and retorts of lead or platinum are usually employed in its production, whilst it must be kept in bottles of lead or indiarubber.

It is largely used for etching patterns upon glass, and for this purpose may be used either as vapour or solution, the latter being preferable as it is much more manageable. In order to etch a drawing upon glass, the surface of the glass is first coated with a thin film of wax, either by warming the glass and brushing over it some melted wax, or else by brushing over it a solution of wax in some volatile solvent. The pattern, etc., to be etched is then drawn upon the wax with a sharp pointed tool, care being taken to remove the wax and expose the surface of the glass in the places to be etched, and a wall of wax having been built round the side of the plate, the solution of hydrofluoric acid is poured over it, and attacks the exposed glass, whilst it has no action on the wax. The acid is left on the plate for from 5 minutes to half an hour, according to the strength of the solution, the depth to which the etching has gone being ascertained by drawing the point of a needle across one of the lines. When etched to a sufficient depth, the acid is washed off with water, and the wax removed by scraping and washing the plate with turpentine.

In using hydrofluoric acid, care must be taken to avoid its contact with the skin, as it produces very painful wounds. Hydrofluoric acid in solution dissolves all the metals with the exception of gold, platinum, mercury; silver and lead forming fluorides of the metals soluble in water.

The fluorides of the alkalis slowly corrode glass when left in contact with them, and liquids for drawing or writing on glass can be prepared by mixing a solution of ammonic or potassic fluoride with sulphuric acid.

The four elements, fluorine, chlorine, bromine and iodine, exhibit a gradual difference in properties and in their power of combining with other elements, fluorine having the greatest affinity for metals and iodine the least, whilst the stability of the compounds formed in combining with oxygen is in reverse order, iodine forming the strongest compound, whilst fluorine is the only element which does not combine with oxygen, and this gradual gradation of affinity is also accompanied by a gradation in physical properties.

	Fluorine	Chlorine	Bromine	Iodine.
Atomic weight	19	35·5	80	127
Physical state	gas	gas	liquid	solid.
Colour	colourless	yellow	brown	black.
Boiling point ...	...	−33°	+63°	+200°
Fusing point ...	...	...	... −7°	+113°

CHAPTER XIX.

SILICON AND ITS COMPOUNDS.

Silicon—Silicon hydride—Silica or silicon dioxide—Occurrence and importance in Nature—Silicic acid—Dialysis—Silicates—Glass—Composition of glass—Manufacture of glass—Silicate of alumina—Clay—Pottery—Porcelain—Stoneware—Bricks—Building stones—Decay of building stones—Granites—Sandstones—Limestones—Dolomite—Mortar—Cements—Silicon tetrafluoride—Hydrofluosilicic acid—Boron.

QUARTZ was believed to be an element until in 1813 Sir Humphrey Davy succeeded in decomposing it and demonstrated that it was the oxide of an element called silicon, which can be obtained by acting on a compound called potassic silicofluoride at a high temperature with sodium or potassium, which combines with the fluorine to form fluoride, whilst the silicon is set free, and on treating the mass with water the fluorides are dissolved and the silicon left as a brown amorphous powder.

$$\overset{\text{Potassic silicofluoride}}{K_2SiF_6} \quad + \quad \overset{\text{Potassium}}{2K_2} \quad = \quad \overset{\text{Potassic fluoride}}{6(KF)} \quad + \quad \overset{\text{Silicon.}}{Si.}$$

Silicon is not acted upon by any acid except hydrofluoric, with which it forms silicon fluoride and hydrogen is evolved—

$$\overset{\text{Silicon}}{Si} \quad + \quad \overset{\text{Hydrofluoric acid}}{4(HF)} \quad = \quad \overset{\text{Silicon fluoride}}{SiF_4} \quad + \quad \overset{\text{Hydrogen.}}{2H_2.}$$

It burns with considerable brilliancy in air or oxygen gas, forming silica (SiO_2), which fuses on its surface and stops the combustion.

Silicon has an atomic weight of 28.

If the potassic silicofluoride is fused with potassium and zinc, the silicon as it is liberated dissolves in the molten zinc, and on cooling deposits in the mass as black shining crystals, which can be separated from the zinc by acting upon the mass with hydrochloric acid and afterwards separately with nitric and hydrofluoric acids which dissolve the metal but leave the crystals of silicon unaltered.

The crystals consist of black shining octahedra, having a specific gravity of 2.49 and are excessively hard. They will not burn in oxygen and are unaffected by acids, except a mixture of hydrofluoric and nitric acids. When heated in chlorine gas, silicon forms a chloride, and nitrogen also enters into direct combination with silicon at high temperatures to form silicon nitride.

In many of its properties silicon very closely resembles carbon, but unlike carbon it only forms one compound with hydrogen, which catches fire spontaneously on coming in contact with air.

Silicon hydride or siliciuretted hydrogen is prepared by fusing anhydrous magnesic chloride with sodic silicofluoride and sodium, together with a flux of salt. The mixture is heated until the sodium flame ceases to be visible, and on allowing the mass to cool, and breaking it out of the crucible used, a grey mass of magnesic silicide is found at the bottom, with a layer of fused chloride and fluoride of sodium above it; and if the magnesium silicide is now roughly powdered and is treated with dilute hydrochloric acid, silicon hydride is evolved which fires spontaneously on contact with air and burns with a bright flame, giving off white fumes consisting of silica (SiO_2), also called silicic acid and silicon dioxide. Silica is by far the most important compound which this element forms, and constitutes a large portion of the crust of the globe.

The purest form of silica is called rock crystal, from its transparency, and occurs crystallised in six sided prisms generally terminating in six sided pyramids, and these crystals coloured by various metallic oxides, form various precious stones such as the amethyst, jasper, agate, cats eye, onyx, opal, chalcedony, carnelian, etc. Silver sand is nearly pure silica, whilst the ordinary forms of yellow sand are silica coloured with iron.

Flint is a form of silica, found in the chalk formation, and silica also is one of the chief constituents of many forms of rock. Most forms of silica are intensely hard, rock crystal scratching glass nearly as easily as the diamond; and all ordinary natural forms of silica are insoluble in water. Silica, however, is found dissolved in certain springs, whilst its presence in straw, bamboo canes, and other vegetable fibres, shows that under some conditions it must be soluble.

If silica is fused with sodic carbonate, a glassy mass called sodic silicate is formed which is soluble in water, and if hydrochloric acid is added in excess to the solution, a semi-solid gelatinous mass of silicic acid is formed; if, however, instead of adding strong hydrochloric acid to the solution of sodic silicate, the sodic silicate be poured into a very dilute solution of hydrochloric acid, this silicic acid will remain in solution together with sodic chloride and hydrochloric acid.

The mixture is then placed in a vessel having a bottom made of vegetable parchment, and this is floated on a bowl of clean, pure water, and under these conditions it is found that substances like salt or hydrochloric acid, will undergo a process of diffusion through the vegetable parchment. and will mingle with the water in the bowl, whilst other substances like silicic acid are unable to penetrate the parchment, and remain behind in the floating vessel.

This method of separating certain substances is called "dialysis," and the floating vessel with the vegetable parchment bottom, is called a "dialyser."

Crystallisable soluble substances like sodic chloride have the power of diffusing through parchment, and are called "crystalloids" to distinguish them from substances like silicic acid, gum, gelatine, albumen, starch, etc., which cannot pass through the parchment, and which are called "colloids."

Treating the mixture of silicic acid, sodic chloride and hydrochloric acid in this way, the sodic chloride and hydrochloric acid diffuse out into the pure water, and water diffuses in to the silicic acid, and if the water in the bowl be frequently changed, in a few hours a perfectly pure aqueous solution of silicic acid will remain in the dialyser.

If this solution be allowed to concentrate over sulphuric acid in a vacuum, it is converted into a gelatinous mass when it contains about 14 per cent. of silicic acid, and this shrinks and gives off more moisture until a glass-like mass having the composition (H_2SiO_3) is left. This substance will not again dissolve in water and is but slightly soluble in hydrochloric acid, and if it is heated so as to expel all water, it becomes totally insoluble in the acid.

When sand is fused with various metallic oxides or carbonates, combination takes place, and the compounds known as silicates are formed, very few of which in composition show that they are formed from the acid (H_4SiO_4), most of them being irregular combinations of the metallic oxide with SiO_2.

Glass is a mixture in varying proportions of silicates of potash, soda, lime, lead oxide, baryta, magnesia, and alumina. If silica, which occurs nearly pure in Nature as silver sand and quartz, is fused at a high temperature with sodic carbonate, a glassy mass of sodic silicate is obtained; but this is slowly acted upon and dissolved by water, and is therefore useless as glass, for it would be incapable of resisting the moisture in the atmosphere; but if a small quantity of lime or oxide of lead is fused with it, a glass is obtained which will resist almost entirely atmospheric influences.

The readiness with which glass will fuse depends upon the silicates it contains, the presence of lead, for instance, causing the glass to melt at a lower temperature than a glass containing lime.

Plate glass and ordinary window glass consist chiefly of silicates of lime and soda.

Bohemian glass is a double silicate of potash and lime, the more fusible kind required for making ornaments, vases, etc., containing also silicate of alumina. Flint glass, of which tumblers, wine glasses, etc., are made, consists of a double silicate of potash and lead; it is called flint glass because the silica used in its composition consists of ground flints.

Window glass is made by fusing together at a high temperature 100 parts of sand with about 35 parts of sodic carbonate and 35 parts of chalk (calcic carbonate). The sand, which is silicic acid, expels the carbon dioxide as gas from the carbonate of soda and calcic carbonate, and silicates of sodium and calcium are formed.

On the manufacturing scale this is done by heating the ingredients together to a temperature, just short of fusion, in a fireclay crucible, which causes the carbon dioxide to be slowly evolved, and prevents frothing over when complete fusion is reached. This first process is called "fritting," and when it is completed the temperature is raised and fusion takes place, the escape of the last portions of carbon dioxide keeping the liquid in agitation, and helping to promote the mixture of the ingredients.

Sometimes sulphate of soda is used instead of the carbonate, but it is then necessary to add a small proportion of charcoal to reduce the sulphur trioxide to sulphur dioxide, which is more easily expelled as gas. The molten mixture is kept for some time in the fused state, so that the air and carbon dioxide bubbles may have time to escape, and the foreign substances, consisting of undecomposed materials and impurities, may rise to the surface as a scum. The temperature is then allowed to slowly fall, and the glass assumes a pasty consistence, in which state it may be readily shaped, at pleasure, into the required form. The workman then plunges an iron tube into the mass, and by taking it out, allowing it to slightly cool and redipping, he collects a quantity of about seven to nine pounds weight, which is then rolled into a pearlike shape on an iron plate. By blowing down the tube whilst causing it to rotate, this is blown out into a large flask shaped bulb, on the bottom of which another rod is attached by means of a bleb of glass, and the neck of the flask is then detached from the blowing tube, and is held in an opening of the furnace, called the nose hole, where it soon begins to melt, the workman then causes the rod with the flask attached to revolve rapidly, when by centrifugal force, the flask opens, and is transformed into a flat circular sheet of what is known as crown glass. At one time all window glass was made in this way, but the method is now nearly abandoned, as the glass so produced can only form panes of very limited size, in consequence of the central lump and of the circular form of the plate.

Sheet glass, which has to a certain extent taken the place of crown glass, is made by blowing a long spheroidal bottle, which, when the ends are cut off, leaves a large cylinder of glass; this is split down one side by touching it with a wet rod, and is then again softened in the furnace, and spread out flat upon an iron plate, giving a sheet of glass, which is less brilliant than crown glass and the surface being wave-marked, has to be worked up by grinding and polishing.

Plate glass, which is now most used, is formed from a mixture of 300 parts of pure silver sand, 100 parts of sodic carbonate, 15 parts of lime, and 300 parts of broken fragments of glass called "cullet," and a little white arsenic. The mixture when fused and converted into glass, is poured on to a heated metal table, and is spread out to the required thickness by means of a heavy metal roller, and is afterwards placed in the annealing oven, where it remains for a week or a fortnight.

The annealing oven is first heated to a dull red heat, and after all air openings have been closed it is allowed to slowly cool down to the temperature of the surrounding atmosphere. The plates are then taken out, ground true and polished and are fit for use.

The process of annealing is of the greatest importance, as if glass is allowed to cool too rapidly, it is liable to crack and fly to pieces.

The glass of which wine bottles are made is of the commonest description; consisting of silicate of lime mixed with the silicates of the alkalis, and of iron and alumina, and it is to the iron present that it owes its dark colour.

When glass has been heated to the softening point and is kept at that temperature for some time without fusion, and then allowed to cool, it is found to be converted into a white opaque mass, much resembling china, which is called "Réaumur's porcelain." This change is called "devitrification," and is due to the crystallisation of the silicates contained in the mass. Many materials are used to colour glass: in painted glass the colouring matter is merely laid on and then burnt in to the surface of the glass, whilst in stained glass the colouring matter is mixed with the ingredients during manufacture. The ornamentation of cut glass is effected by grinding it, and designs are etched upon it by means of hydrofluoric acid, which dissolves out the silica from the glass, in this way eating into it.

One of the most important natural silicates is silicate of alumina, which is the basis of all clays and also occurs in a more or less pure condition in slate, pumice stone and fuller's earth.

Clay varies very much in composition, china clay or kaolin being nearly pure hydrated silicate of alumina, whilst the commoner kinds of yellow clay contain considerable quantities of iron. The plastic properties of the different kinds of clay render it specially adapted for moulding into various forms; its use for the manufacture of pottery dates from a very early period in the world's history.

If a well kneaded specimen of clay be chosen it may be readily moulded into any required form, but when heated it has the property of shrinking; so that on baking, the vessel would crack and lose its shape. To obviate this, it is mixed with a certain proportion of sand, chalk or bone ash, which prevents shrinkage, but renders the baked vessels very brittle; to overcome this difficulty, some "felspar" (a silicate of alumina and potash) is added, which fuses at the temperature employed in baking the ware, and thus forms a cement, which binds the particles of infusible clay into a compact mass. The vessel made of this mixture, when baked, retains its shape and does not crack, but it has the disadvantage of being porous, and is therefore unfit for ordinary use. To prevent this it must be glazed, that is, coated with some easily fusible material, which will form a thin coating of glass on the surface.

In the manufacture of porcelain, 62 parts of kaolin, 4 parts of chalk, 17 parts of sand and 17 parts of felspar are ground to the finest possible powder in water, and are allowed to stand until the coarser particles have settled down to the bottom of the grinding vat. The creamy fluids containing the finer particles in suspension are then mixed in the proper proportions and are allowed to settle; the sludge deposited at the bottom is then drained until it reaches the right consistence, and is then thoroughly mixed and kneaded. The paste, so prepared, is now ready for making porcelain, but it has been found that it improves greatly by keeping for a considerable space of time in a damp place, the organic impurities which it contains being destroyed. Before the paste is used for moulding, it is again worked up and kneaded by hand.

The moulds used in the process of shaping are always made of a porous material, capable of absorbing the moisture from the clay, generally plaster of Paris. When the pattern is very complex, the mould is made in several pieces, but for round objects it is made in two parts. When the paste has been sufficiently dried by the absorption of its moisture by the mould, the latter is removed by separating its two halves, leaving the work complete. The articles are then air dried, and afterwards packed in cylindrical cases of refractory clay, which are then arranged in a furnace or kiln and baked, the temperature being allowed to rise very gradually.

When sufficiently baked, the "biscuit porcelain," as it is now called, has to be glazed, and this is done by dipping it into a very finely ground mixture of felspar and quartz, suspended in vinegar and water. The porous ware absorbs the water, and leaves a coating of felspar and quartz on its surface, which on heating a second time in the kiln, fuses and forms a glaze, partly penetrating the ware, and partly remaining as a varnish on the surface. It is very important that the glaze employed should have the same rate of expansion for heat as the porcelain; otherwise, as it cooled, the glaze would crack.

In colouring wares of this kind, if a uniform tint is required, the materials for producing it are mixed with the glaze; but coloured designs are painted upon the ware after glazing, and are generally composed of coloured glasses, ground with turpentine, which colours, when again heated in the kiln, fuse into the glaze.

Stone ware is a much coarser description of porcelain, containing both iron and lime, to the presence of which it owes it colour and fusibility, and it is covered with a glaze of silicate of soda, which is produced by the process known as "salt glazing." The articles are coated, by dipping, with a thin film of sand, and are then intensely heated in the kiln, into which some damp salt is thrown. The water present is decomposed, its hydrogen taking the chlorine from the salt to form hydric chloride, whilst its oxygen combines with the sodium of the salt to form sodic oxide, which, coming in contact with the silica on the surface of the ware, forms a glaze of sodic silicate.

Staffordshire ware, of which common plates, &c., are made, is manufactured from a description of white clay of less value than kaolin; it is mixed with ground flints, and is fired at a high temperature, and after being dipped in a highly fusible glaze, consisting of oxide of lead, ground flints, and a little clay, it is again fired at a lower temperature.

Earthenware vessels and pipes are made from common clay, mixed with a certain proportion of marl and sand, and they are glazed with a mixture of from four to five parts of clay with six to seven parts of oxide of lead.

Bricks are also made of common clay, mixed when necessary with sand, and they, as in the case of common earthenware, owe their colour to the iron which they contain.

In choosing building materials, those substances should be employed which offer the greatest resistance to atmospheric influences.

The causes which tend to produce decay in building materials are two: First—the disintegrating action of rain and frost; and secondly—the solvent action on certain ingredients of the materials exercised by carbon dioxide, and acid impurities dissolved in rain water or suspended in the moisture present in the air as fog or mist. As a rule, these two factors of decay act together; the weathering action first rendering the surface of the stone rough and porous, and this gives a coign of vantage for the lodgement of the rain with its gaseous impurities, which, dissolving out carbonates of lime and magnesia further disintegrates the surface, and causes scaling and pitting of the stone.

This being the case, it is evident that the smoother and harder the surface of the materials employed the less rapid will be the decay; and also that the vertical walls of a building as they allow the water to freely run off from their surface, will be less exposed to these actions, and will therefore resist them better than ledges and horizontal surfaces, which, holding water, will be acted upon to a greater extent.

This is fully borne out by experience, and in buildings of sandstone and limestone it is nearly always found to be these portions which are first attacked.

It has been noticed that many of the ancient monuments of Greece and Egypt, even now, show but slight traces of decay as compared with the buildings to be found in this country, and the difference is partly due to the greater resistance afforded by the surface of the materials used, and to an even greater extent, to the much smaller quantity of rain which falls in those countries and to the purity of the atmosphere.

The building stones used in this country are:—

1. Granite.
2. Sandstone or freestone.
3. Limestone.
4. Magnesian limestone or dolomite.

Granite is by far the most lasting of the building stones, and consists of from 65 to 80 per cent. of silica, which seems to act as a cement in building together mica and felspar, the whole mass being of a crystalline character. The chief granite yielding districts of England are Devon, Cornwall and Cumberland, whilst Scotland and Wales also furnish large quantities. The Devon and Cornwall granite has been largely used—Westminster, Waterloo and London bridges, the Thames Embankment, the London docks, Keyham docks and the Portland breakwater being built of it; whilst in Scotland the Aberdeen and Peterhead quarries supply some of the most valuable stone, of which the pillars of the Carlton Club and Fishmonger's Hall are built.

The fine surface and power of resisting disintegration possessed by granite, render it the best building stone we possess, but owing to its great hardness, it is so difficult to work, that it is only employed for massive and simple work, where great resistance to wear and tear is required.

The sandstones consist essentially of particles of silica, *i.e.*, sand, which has been probably formed by the disintegration of older rocks, and has collected in deposits, and has been consolidated into a hard mass by the carbonates of lime and magnesia, the percentage of silica present varying from 84 to 93 per cent., whilst the carbonates binding it together vary from less than one per cent. up to nearly 13 per cent.

The sandstones are largely used for building purposes in Scotland, where they are employed to a great extent, especially in Glasgow and Edinburgh, but carbon dioxide dissolved in rain water is able to rapidly dissolve out the cementing carbonates and so cause disintegration of the surface.

The limestones are perhaps those most generally in use, and consist of carbonate of lime, with small and varying quantities of other substances, such as silica and alumina, and their power of resisting the atmospheric influences entirely depends upon their density and compactness of structure.

Marble, which is the most compact form of limestone, will resist the action of the atmosphere for centuries, whilst the more porous kinds are rapidly acted upon.

Portland stone, of which St. Paul's is built, is, next to marble, the most durable, and Bath stone also resists atmospheric action for a considerable period.

Dolomite, or magnesian limestone, is a double carbonate of lime and magnesia, and is much used because it is easily sawn into blocks, and can be readily carved; but it is also readily acted upon by the water and carbon dioxide in the air. The magnesian limestone, of which the Houses of Parliament are built, contains about 50 per cent. of carbonate of lime, 40 per cent. of carbonate of magnesia, and some silica and alumina.

In manufacturing towns much damage is caused by the sulphuric acid in the air, formed by the combustion of coal, containing small traces of sulphur.

Mortar is a mixture of one part of freshly slaked lime with two of sand mixed with water, to the consistence of a thin paste; and the hardening of mortar at first depends upon the conversion of some of the lime into carbonate by the absorption of carbonic acid from the air; whilst, after the lapse of a considerable time, a still further hardening takes place due to the formation of silicate of lime.

Cements or hydraulic mortars are made by heating together very finely divided chalk and clay, when carbonic acid is expelled and silicates of lime and alumina are formed, together with a compound of alumina and lime; and when this cement is mixed with water, combination takes place, the cement setting as a hard mass of hydrated double silicates, upon which more water has no effect.

In the manufacture of Portland cement, instead of ordinary clay, river mud is used. When silica or silicates are acted upon by hydrofluoric acid, or by a mixture of fluor spar and concentrated sulphuric acid, a gas is evolved which fumes in air and has a pungent odour. This gas is a compound of silicon and fluorine and may be looked upon as being silica in which the two atoms of oxygen have been replaced by four atoms of fluorine. It is called silicon tetrafluoride.

$$\overset{\text{Silica}}{SiO_2} + \overset{\text{Hydrofluoric acid}}{4(HF)} = \overset{\text{Silicon tetrafluoride}}{SiF_4} + \overset{\text{Water}}{2(H_2O)}$$

or,

$$\overset{\text{Silica}}{SiO_2} + \overset{\text{Calcic fluoride}}{2(CaF_2)} + \overset{\text{Sulphuric acid}}{2(HSO_4)} = \overset{\text{Calcic sulphate}}{2(CaSO_4)}$$

$$+ \overset{\text{Silicon tetrafluoride}}{SiF_4} + \overset{\text{Water.}}{2(H_2O).}$$

When brought in contact with water, it at once undergoes decomposition with formation of silica, which is deposited, whilst an acid containing hydrogen, silicon and fluorine, called hydrofluosilicic acid is formed :—

$$\overset{\text{Silicon tetrafluoride}}{3(SiF_4)} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Hydrofluosilicic acid}}{2(H_2SiF_6)} + \overset{\text{Silica.}}{SiO_2.}$$

This acid is prepared most conveniently by heating together a mixture of sand, fluor spar, and sulphuric acid in a stoneware bottle, and leading the silicon tetrafluoride produced through a wide delivery tube, dipping into a small cup of mercury placed at the bottom of a vessel of water, thus guarding against obstruction of the exit tube by silica. Each bubble of gas as it passes up through the mercury is decomposed immediately it comes in contact with the water, and after a few hours the water becomes thick with the gelatinous mass of separated silica, and if this be filtered off, the clear filtrate will contain the hydrofluosilicic acid (H_2SiF_6).

Boron is an element which closely resembles silicon ; it is obtained from boracic acid by fusing it with potassium as a brown amorphous powder, which on fusion with aluminium, combines with some of it and forms octahedral crystals resembling the diamond in hardness and power of refracting light. Boron differs from most of the other elements in combining directly with nitrogen when heated to redness forming a nitride.

In certain parts of the volcanic districts of Northern Italy, jets of steam issue with considerable violence from the ground, and are found to contain a compound of hydrogen, boron and oxygen, called boracic acid, which can be obtained in the crystalline form, and which has the composition (H_3BO_3), and is largely used for antiseptic purposes, as it prevents decay and putrefaction. Boracic acid forms a few salts, themost important of which is sodic biborate or borax ($Na_2B_4O_7$), which is used to a considerable extent for cleaning metallic surfaces, from which, when fused, it has the power of dissolving metallic oxides, and also for glazing certain kinds of stoneware.

CHAPTER XX.

PHOSPHORUS.

Extraction of phosphorus from bones—Properties of phosphorus—Amorphous phosphorus — Matches — Wax vestas — Safety matches—Phosphuretted hydrogen or phosphine—Calcic phosphide—Holmes' light—Phosphorus trioxide—Phosphorus pentoxide — Metaphosphoric, pyrophosphoric and orthophosphoric acid—Arsenic—Oxides of arsenic—Arseniuretted hydrogen—Marsh's test—Testing for arsenic—Reinsch's test.

OWING to the intense affinity for oxygen, phosphorus is never found free in Nature, but occurs in large quantities combined with metals of the alkaline earths, the commonest being tricalcic phosphate $Ca_3(PO_4)_2$. By the disintegration of the minerals containing phosphates, the latter pass into the soil, and are absorbed by plants, appearing principally in the seed. The minerals phosphorite, coprolite, and apatite, also contain phosphorus. In the animal kingdom, the element appears to be a very necessary ingredient in the brain and other centres of nervous action; and in bones about 60 per cent. of the total weight consists of mineral phosphate, and it is from the ashes of burnt bones that phosphorus itself is usually obtained.

The following analysis of the bones of oxen, gives a fair idea of the general composition :—

Animal matter	30.58
Calcium phosphate	57.67
Magnesium phosphate	2.07
Calcium fluoride	2.69
Calcium carbonate	6.99

The bones are heated with water under pressure, which dissolves out the ossein or soluble organic matter, and this is either purified for domestic or photographic use, or sent into the market as glue. The mineral matter left is heated to redness in air, and the white ash left behind is called bone ash, and consists chiefly of tricalcic phosphate; this is heated with about two-thirds its weight of strong sulphuric acid. In this way insoluble calcic sulphate, and soluble calcic superphosphate are formed. The latter substance is largely used as a manure for cereal crops.

$$\overset{\text{Tricalcic phosphate}}{Ca_3(PO_4)_2} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)} = \overset{\text{Calcic superphosphate}}{CaH_4(PO_4)_2} + \overset{\text{Calcic sulphate.}}{2(CaSO_4)}.$$

The mass is then filtered through linen, which separates the calcic sulphate, and the soluble superphosphate is mixed with charcoal and evaporated nearly to dryness in leaden pans. This residue is finally heated to redness in an earthenware retort, the neck of which dips into water. The first effect of the heating is to convert the superphosphate into calcic metaphosphate, water being driven off, thus :—

$$\overset{\text{Calcic superphosphate}}{CaH_4(PO_4)_2} = \overset{\text{Calcic metaphosphate}}{Ca(PO_3)_2} + \overset{\text{Water.}}{2(H_2O)}.$$

On heating still further carbon monoxide is given off and the phosphorus distils over, thus :—

$$\overset{\substack{\text{Calcic}\\\text{metaphosphate}}}{3Ca(PO_3)_2} + \overset{\text{Carbon}}{5C_2} = \overset{\substack{\text{Tricalcic}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \overset{\substack{\text{Carbon}\\\text{monoxide}}}{10CO} + \overset{\text{Phosphorus.}}{P_4}.$$

The phosphorus so obtained is thick and opaque from the presence of impurities, and is again melted under warm water and squeezed through washleather; sometimes also if very impure, it is heated with a mixture of potassium dichromate and sulphuric acid, and after well washing is melted and cast into sticks under warm water, or if for match manufacture into cheese shaped masses.

The phosphorus so obtained is almost colourless and transparent, but when exposed to light it gradually acquires an opaque red coating, partly due to its conversion into a suboxide of phosphorus and partly to the formation of the red variety of the element phosphorus.

It has an intense affinity for oxygen and for this reason has to be kept under water, as it inflames at a temperature of 44° C. It is soluble in bisulphide of carbon and also in chloride of sulphur—if the solution in bisulphide be allowed to stand in contact with air, the solvent evaporates off and leaves the phosphorus in so fine a state of division that it spontaneously ignites.

If ordinary phosphorus be kept at a temperature of 230° C. for some hours, in an atmosphere of gas incapable of acting chemically upon it, such as nitrogen or carbon dioxide, it gradually changes to a dark red mass, having the same chemical composition but totally distinct in all its properties from yellow phosphorus. It undergoes no change when exposed to air or light and may be heated to 250 °C. before it ignites, at which temperature it is reconverted into ordinary phosphorus. Unlike the ordinary phosphorus it is insoluble in carbon bisulphide, unattacked by chlorine or iodine at ordinary temperatures and nonpoisonous. Having no vestige of crystalline structure, it is sometimes called " amorphous " phosphorus.

The density of phosphorus is 62, and its molecular weight is therefore 124, but it can be proved from its hydrogen compounds that the atomic weight of the element is 31, and it follows therefore that the molecule consists of 4 atoms, and inasmuch as dissociation does not take place even at 1040° C., it is evident that the molecule has this composition. Phosphorus enters largely into the composition of the paste with which lucifer matches are tipped.

In the manufacture of lucifer matches, even grained white pine is taken and is dressed and sawn into blocks of the required size, which are then split up by machinery into splints twice the length of the matches to be made; these are then wound round and round by machinery with a thick woollen or leather band, which leaves an inch of splint projecting at each end, and the thickness of which separates the splints one from the other. Several thousand splints having been in this way rolled up into a firm compact bundle, not unlike a small millstone in size and shape, they are passed on to a man who places them on a flat metal plate, and pats the projecting ends with a flat wooden tool until the ends are all level; the bundles are then passed with one set of ends downward, over hot plates to warm the wood, and are then dipped in shallow pans containing melted paraffin wax; the bundles are then turned over, passed on over more hot plates, and the other ends then dipped. By the time the bundles are taken from this department, to the portion of the factory where they are to be tipped with the phosphorus composition, the paraffin has hardened and they are ready for the next process, which consists of tipping them with the match composition made by mixing phosphorus and either potassic nitrate or chlorate, red lead, peroxide of lead, or manganese dioxide, together with gum or glue enough to make a thin paste, to which sometimes some colouring matter, such as vermilion or Prussian blue is added.

In such a composition, there is present the highly inflammable phosphorus and a compound containing oxygen, and friction is sufficient to set up chemical action between the two—the heat evolved by the combination of the phosphorus and oxygen to form phosphoric pentoxide being sufficient to inflame the paraffin or sulphur on the splint, and this in turn ignites the wood.

The amount of phosphorus present in the mixture varies very much according to the method employed in mixing it with the composition—in some cases not more than 5 per cent. being present, while sometimes the quantity rises to 30 per cent. Too much phosphorus in the mixture is to be avoided, as besides being costly it defeats its own purpose by producing a large quantity of the pentoxide, which coats the end of the match and so retards and even prevents ignition of the splint.

In England, potassic chlorate is generally used as the oxidising agent, such mixtures generally detonating slightly when the matches are struck, whilst on the continent potassic or lead nitrates and a little red lead or peroxide of lead are often used instead, these matches igniting quietly and being known as "silent matches."

If phosphorus, even in the amorphous state is mixed with potassic chlorate, it forms a most dangerous explosive which detonates violently on subjection to the lightest friction or blow, but in the match mixture the particles of phosphorus and chlorate are coated with the glue used, and are thus preserved from intimate contact until friction is applied.

The match mixture is spread as a thin paste on tables made of iron, and heated by steam, the depth of mixture being gauged by a thin rim over which a flatting tool is passed. The ends of the splints already coated with paraffin, are dipped in the mixture, and the wheels of splints are strung on spindles in small fire-proof chambers to dry, a rapid draught of warm air being created by revolving fans. When dry the bundles are unrolled by machinery and taken to the "boxing" benches, where women take a handful of the matches, cut them in half by means of a sharp hinged knife, and pack them into the boxes with marvellous rapidity.

At this stage of the operations, firing of the matches often takes place during frosty weather, when the air is crisp and dry, but under ordinary atmospheric conditions the loss from this cause is very small.

Bryant and May's "safety matches" contain no phosphorus in the head of the match, the tipping mixture consisting of antimony trisulphide, potassic chlorate and powdered glass, mixed into a paste with glue.

This mixture will explode when struck a sharp blow, and will ignite when subjected to very great friction, a long steady stroke across a sheet of glass being sufficient to ignite the safety matches, but they are not sufficiently sensitive to ignite with ordinary friction, doing so at once however, when rubbed against the composition on the side of the box which contains amorphous phosphorus mixed with glass.

The manufacture of safety matches is in all respects the same as that described above, with the exception of the composition of the mixture used for the tips.

In the manufacture of wax vestas, cotton is wound off from the hank and is passed in bundles of about a dozen strands through a melted mixture of stearine, containing either paraffin wax or gum dammar to harden it; the cotton is passed through several times until it has taken up the required amount of the wax mixture, and is then made uniform in size, and polished on the outside by passing through a warm metal plate pierced with holes of the required size.

At Messrs. Bryant and May's manufactory, 800 miles of this taper can be made in a day.

The taper is then passed on to the cutting machine, where in one operation it is cut to the required length for the matches, and clamped in frames with thin wooden battens between the rows, each frame holding 7,200 matches; the frames are then taken to the dipping table, dipped in the mixture, dried in racks in fireproof chambers, and are then ready to be unpacked from the frames and put in the boxes.

In all accounts of the match industry great stress is laid upon the painful and disfiguring diseases of the bones of the face induced by constant contact with the fumes of phosphorus in a match factory, but of late years it has been found that attention to cleanliness of person amongst the operatives does away, to a great extent, with what undoubtedly was a great evil, and in such factories as Messrs. Bryant and May's, where scrupulous cleanliness is enforced, it has practically disappeared. Red amorphous phosphorus, as it does not give off fumes, tends to reduce the danger, but in nearly all factories a larger quantity of ordinary, than red phosphorus is still used.

Many attempts have been made, from time to time, to do away with the use of phosphorus in matches, but the action of the compounds used (which generally contain antimony sulphide, and chlorate of potash as a basis) is not sufficiently certain to lead to their general adoption.

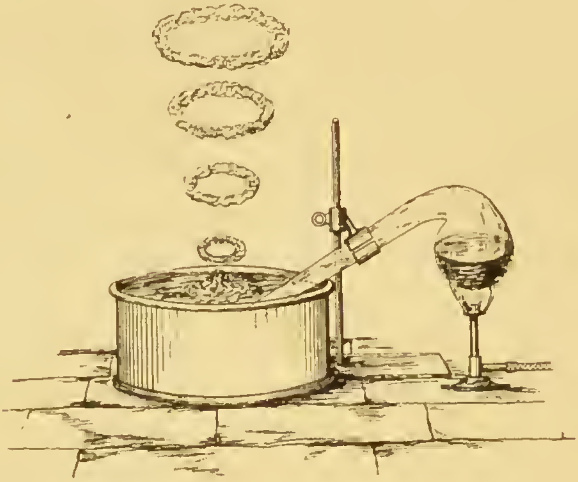

Fig. 52.

Phosphorus does not directly combine with hydrogen, but by indirect means, three compounds can be obtained, only one of which, however, is of any practical importance. Hydric phosphide, phosphuretted hydrogen or phosphine, consists of hydrogen and phosphorus combined together in the proportion of 31 parts by weight of phosphorus to 3 of hydrogen, to which the formula (PH_3) has been assigned.

A few pieces of ordinary phosphorus are placed in a retort (Fig. 52) which is then entirely filled with a solution of sodic hydrate; if its mouth be placed under the surface of water and the retort and its contents heated a gas is evolved which, having filled the neck of the retort, escapes a bubble at a time, and each bubble as it comes in contact with air, spontaneously inflames with a flash of white flame and formation of rings of smoke, consisting of phosphoric pentoxide formed by the combustion of the phosphorus with the oxygen of the air. If instead of allowing the gas to escape into air, it is collected in a cylinder over water, it will be seen to contain some oily drops and also will deposit a yellow solid on the side of the cylinder. The liquid and solid are the other two "phosphines," the liquid having the composition (P_2H_4), and the solid the probable composition (P_4H_2), and it is to the presence of the liquid compound that the spontaneous inflammability of the phosphuretted hydrogen is due.

The formation of the gas may be represented as follows:—

$$\overset{\text{Phosphorus}}{P_4} + \overset{\text{Sodic hydrate}}{3(NaHO)} + \overset{\text{Water}}{3(H_2O)} = \overset{\text{Sodic hypophosphite}}{3(NaH_2PO_2)} + \overset{\text{Phosphuretted hydrogen.}}{PH_3.}$$

If the evolved gas is passed through a tube cooled by a freezing mixture, the liquid phosphine condenses, and the phosphuretted hydrogen loses its power of igniting spontaneously. The phosphine can also be removed by employing an alcoholic solution of potash, instead of an aqueous solution, when it is absorbed and kept back by the alcohol.

When quicklime and phosphorus are heated to bright redness in an air tight crucible, or the vapour of phosphorus is passed over heated quicklime, a dark brown solid is obtained containing calcic phosphide. If this substance be thrown on to water, it decomposes with formation of liquid phosphine.

$$\overset{\text{Calcic phosphide}}{2(CaP)} + \overset{\text{Water}}{4\,H_2O} = \overset{\text{Calcic hydrate}}{2Ca(HO)_2} + \overset{\text{Phosphine.}}{P_2H_4.}$$

The liquid phosphine is very unstable and at once splits up into the solid phosphine and phosphuretted hydrogen, which ignites on coming into contact with the air.

Calcium phosphide rapidly deteriorates when exposed to air, being partially decomposed by the moisture present in it. This substance is used in "Holmes' lights," which consist of sealed cartridges containing calcium phosphide. To use them the seal is torn off and they are attached to the torpedo or other object, the position of which is to be made visible when in the water. The water decomposes the phosphide and the flash of the burning phosphuretted hydrogen reveals the whereabouts of the floating object at night, whilst the heavy white smoke serves as a guide by day.

Phosphuretted hydrogen is a colourless gas with a very disgusting odour, resembling putrid fish. Its molecular weight is 34 and density 17.

In composition it resembles ammonia gas, and forms compounds analogous to those of ammonium. For instance, it combines with hydric iodide (HI) to form phosphonium iodide (PH_4I) corresponding to ammonium iodide (NH_4I).

Phosphorus forms two well defined oxides, viz.:—

Phosphorus trioxide, P_2O_3.
Phosphorus pentoxide, P_2O_5.

Phosphorus trioxide is a white, deliquescent powder formed by the slow oxidation of phosphorus in a limited supply of dry air. If the trioxide be heated to a high temperature in a sealed tube, it forms phosphorus pentoxide and phosphorus.

The trioxide dissolves in water to form phosphorous acid:—

$$\underset{\text{Phosphorus trioxide}}{P_2O_3} + \underset{\text{Water}}{3(H_2O)} = \underset{\text{Phosphorous acid.}}{2(H_3PO_3)}.$$

The solution is a very powerful reducing agent.

Phosphorus pentoxide (P_2O_5) is formed when phosphorus is burnt in dry air or oxygen; it is a white flaky solid having an intense avidity for moisture. If left exposed to air, it rapidly deliquesces and is used as a dehydrating agent as it will abstract moisture from nearly all bodies which contain it, even sulphuric and nitric acids being dehydrated by it.

It may be sublimed unchanged, and when heated with charcoal it breaks up into phosphorus and carbon monoxide.

The pentoxide combines with water in three proportions, forming:—

Metaphosphoric acid, $P_2O_5H_2O = 2(HPO_3)$
Pyrophosphoric acid, $P_2O_52(H_2O) = H_4P_2O_7$
Orthophosphoric acid, $P_2O_53(H_2O) = 2(H_3PO_4)$.

Of these three acids the most important is orthophosphoric acid, or ordinary phosphoric acid (H_3PO_4). It is tribasic, and forms three classes of salts, as—

Monosodic orthophosphate = NaH_2PO_4
Disodic orthophosphate = Na_2HPO_4
Trisodic orthophosphate = Na_3PO_4.

The atoms of hydrogen can also be replaced by different monad metals as in microcosmic salt, which is hydric ammonic sodic phosphate (H,NH_4NaPO_4).

If orthophosphoric acid be heated to 215°, two molecules lose one molecule of water, and pyrophosphoric is formed, thus:—

Orthophosphoric acid		Water		Pyrophosphoric acid.
$2(H_3PO_4)$	=	H_2O	+	$H_4P_2O_7$.

This acid is tetrabasic, and forms four series of salts with monad metals.

If the orthophosphoric acid be heated to redness, one molecule of the acid loses one molecule of water and metaphosphoric acid is formed, thus:—

$$\overset{\text{Orthophosphoric acid}}{H_3PO_4} = \overset{\text{Water}}{H_2O} + \overset{\text{Metaphosphoric acid.}}{HPO_3}.$$

This acid is also prepared by dissolving the pentoxide slowly in water. It is monobasic and forms only one class of salts. All these acids are deliquescent and very soluble in water. They are distinguished by the following tests:—

Orthophosphoric acid, when neutralised, gives a white precipitate with barium chloride, and a yellow one with silver nitrate. Neither the acid nor any of the salts coagulate albumen.

Pyrophosphoric acid does not coagulate albumen, and gives white precipitates with silver nitrate and with barium chloride, only in neutral solutions.

Metaphosphoric acid coagulates albumen and gives a white precipitate with barium chloride or silver nitrate.

Chlorine readily combines with phosphorus to form the trichloride (PCl_3). It is a colourless fuming liquid, decomposed by water into phosphorous and hydrochloric acids:—

$$\overset{\substack{\text{Phosphorus}\\ \text{trichloride}}}{PCl_3} + \overset{\text{Water}}{3(H_2O)} = \overset{\substack{\text{Hydrochloric}\\ \text{acid}}}{3(HCl)} + \overset{\substack{\text{Phosphorous}\\ \text{acid.}}}{H_3PO_3}.$$

The trichloride readily absorbs chlorine to form phosphorus pentachloride (PCl_5), which is a yellowish crystalline solid. If this substance be exposed to moist air, it forms phosphorus oxychloride ($POCl_3$).

Arsenic ($As = 75$) is often classed amongst the metals on account of its lustre and other physical properties which it possesses. It is incapable of forming a base with oxygen, and the general character of its chemical combinations justifies its consideration with the nonmetals. Being a complete analogue of phosphorus, it is best studied after that element.

The element is found in combination with iron, as mispickel (FeS_2FeAs_2), also as realgar (As_2S_2), and yellow orpiment

(As_2S_3). The ore is roasted, and the fumes of arsenic trioxide which are collected, are reduced with charcoal in covered crucibles, arsenic subliming in the upper part of the apparatus.

Arsenic oxidises slightly in moist air, is very brittle and crystalline. At 180° C. it volatilises without fusion, and its vapour density is twice as great as its atomic weight, consequently its molecule is assumed to contain 4 atoms instead of two. The vapour has the peculiar odour of garlic.

On heating, arsenic readily combines with oxygen to form the trioxide (As_2O_3). Arsenic trioxide dissolves to a small extent in water to form arsenious acid (H_3AsO_3), but this is not known in the free state. It combines with metals to form arsenites.

If arsenic or trioxide of arsenic be warmed with nitric acid, the pentoxide is formed (As_2O_5). This oxide combines with three molecules of water to form arsenic acid, which forms salts called arsenates, corresponding to the phosphates.

Arsenic trioxide, or white arsenic, is employed in the manufacture of glass, in the preparation of colouring matters, as a constituent of sheep dipping compositions, fly papers, vermin killers; and is sometimes used as arsenical soap for the preservation of skins and objects of natural history.

Commercial white arsenic is a fine white powder so closely resembling flour in appearance that it has occasionally been substituted for it, with disastrous results—notably, where it was introduced as a constituent of toilet powder in place of fine starch. It is, however, so heavy (sp. gr. 3.8) that it can easily be distinguished from flour, and under the microscope is seen to consist of glassy crystalline fragments.

White arsenic is, fortunately, only very slightly soluble in water; a cold saturated solution only containing 2.5 grams of the oxide in a liter of water. In event, then, of the oxide being thrown into water, but little dissolves; and if the mixture be stirred and swallowed, the insolubility of the oxide aids the treatment by antidotes, the chances of success being greater than in the case of easily soluble metallic poisons. The smallest dose, attended with fatal results, is about two grains.

The employment of arsenic as a constituent of green colouring matters is now, happily, to a great extent, a thing of the past; but it has been recklessly employed in wall papers, lamp shades, and even as a colouring matter for confectionery.

If zinc, alloyed with arsenic, be acted on by dilute sulphuric acid, the hydrogen given off is mixed with an excessively poisonous gas called, arsenetted hydrogen (AsH_3). This gas is readily decomposed on heating, metallic arsenic being deposited. It burns with a livid flame forming arsenic trioxide and water. If a cold surface be depressed on the flame, so as to lower the temperature of the gas, a mirror of arsenic is obtained (Marsh's test).

If arsenious acid be distilled with strong hydrochloric acid, arsenious chloride is obtained ($AsCl_3$). This affords an excellent method of determining the presence of arsenic in wall paper, fabrics, &c. The paper, about 6 inches square, is cut into strips, and boiled with strong hydrochloric acid in a retort, the distillate is diluted with water and sulphuretted hydrogen gas passed through. If any arsenic be present, a yellow precipitate of the sulphide (As_2S_3) will be obtained. This method, however, is useless in determining the presence of arsenic when mixed with organic matter, on account of the frothing up of the mixture when boiled. The simplest way is to acidify with hydrochloric acid, place in the mixture a sheet of clean copper, and warm gently. If any arsenic be present, it will be deposited on the copper. To determine its presence, the copper is carefully wiped and dried, and heated in an open tube. The arsenic will oxidise to trioxide and the crystals formed can be dissolved and tested in the usual way (Reinsch's test).

CHAPTER XXI.

THE METALS.

Metallic properties—Occurrence of metals in Nature—Processes by which the common metals are obtained from their ores—Conductivity of metals for heat and electricity—Melting points—Specific gravitics—Tenacity, malleability and ductility—Grouping of the metals—Potassium—Sodium– Salts of sodium—Bay salt—Sodic carbonate—Manufacture of sodic carbonate—Barium—Strontium—Calcium—Salts of calcium—Calcic carbonate—Quick lime—Calcic sulphate—Plaster of Paris—Spectrum analysis—Fraunhofer's lines—Absorption spectra.

THE elements are for the sake of convenience divided into two groups, the nonmetallic elements and the metallic; but it must be clearly borne in mind that no natural line of demarcation of this kind exists, and that the properties of the elements exhibit a gradual transition from those elements which are unmistakably nonmetallic in their characteristics to those which have equally definite metallic properties, so that with certain elements, such as arsenic, a certain amount of doubt exists as to which division it should belong.

Physically, metals are recognised by their lustre and power of conducting heat and electricity, whilst the chemical definition of a metal is "an element capable of forming a base by union with oxygen."

Nearly all the metals used in the arts and manufactures are found in Nature combined with other substances; indeed, gold and platinum, both of them rare metals, which are practically unacted upon by other elements, or compounds, are the only exceptions to this; the remaining metals, although small quantities may be sometimes found uncombined, practically existing only in combination. If we take a piece of iron and expose it to the action of moist air, the iron rusts, that is becomes finally converted into a compound of iron with the oxygen of the air, called oxide of iron; the whole of the original metal being eaten away if exposed for a sufficiently long period. Again, if we leave a silver vessel exposed to the air, it slowly becomes tarnished, due to the formation of sulphide of silver on its surface, caused by traces of sulphuretted hydrogen in the atmosphere. It is therefore evident that our ordinary metals are in a more or less unstable condition, and, if left to themselves, are always ready to unite with certain other substances to form compounds; and it is for this reason that no large amount of these metals is ever found in a pure state in Nature.

The native compounds of the metals we call minerals or ores, and the art of extracting metals from their ores we call "metallurgy."

The principal ores are as a rule oxides, sulphides, carbonates, arsenides, and silicates of the metals, and have most of them been formed at a high temperature. These compounds hardly ever occur in a separate state, but are more or less mixed with other minerals, and in nearly all metallurgical operations, the ore from which the metal is to be extracted has to undergo several mechanical operations in order to free it as far as possible from these extraneous matters, before it can be subjected to the particular chemical operations which isolate the metals from the elements with which they are combined.

In all the metallurgical processes which are here considered the chemical actions taking place are aided by the action of heat, and these actions may be divided into two classes, roasting and smelting; and the *roasting* may be either (*a*) *roasting and reducing*, as when oxide of iron is heated to a temperature short of its melting point in contact with gases capable of abstracting its oxygen and leaving metallic iron; or (*b*) *roasting and oxidising*, as when sulphide of copper is roasted in a current of air, when the oxygen of the air converts some of the sulphur into sulphur dioxide, and some of the copper into oxide of copper. The reducing or oxidising nature of the action being determined by the kind of furnace used and the proportions of air, fuel, and ore taking part in the operation.

In roasting operations the temperature employed is not allowed to rise to the melting point of the materials used, but in *smelting* sufficient heat is generated to melt the substances employed, and in the liquid state they then react upon one another, forming new compounds, and in some cases liberating the metal, as when oxide, sulphide, and sulphate of lead are melted together and produce metallic lead with escape of sulphur dioxide.

By the term "oxidation" we imply an action in which the oxidisable element or compound combines with the element oxygen, as when iron rusts, or carbon burns in oxygen gas. While the term "reduction" means the abstraction from a compound, of oxygen or some element resembling oxygen in its behaviour, such as sulphur: as for instance when oxide of copper is heated in a stream of hydrogen gas, the hydrogen takes the oxygen from the copper oxide to form water and "reduces" the copper oxide to metallic copper.

In all manufacturing processes, the most valuable reducing agent in use is carbon; as used in the form of coke, charcoal, or coal, it can be made not only to supply the heat necessary for roasting or smelting, but also by its partial combustion to form a gas called carbon monoxide having great reducing properties.

With the exception of mercury, all the metals are solid at ordinary temperatures, and most of them have definite crystalline structure, and are possessed of a certain power of reflecting light called metallic lustre, which however they exhibit only when in compact masses, and not when in a fine state of division.

Metals are all conductors of electricity, and silver being the best, is taken as the standard, its conductivity being represented as 100, and they also possess the power of conducting heat in nearly the same order, so that a good conductor of heat is generally also a good conductor of electricity.

CONDUCTIVITY OF THE COMMONER METALS FOR HEAT AND ELECTRICITY.

Metal.	Heat.	Electricity.
Silver	100	100
Copper	73.6	77.4
Gold	53.2	55.9
Tin	14.8	17.0
Iron	11.9	14.4
Lead	8.5	7.7
Platinum	8.4	10.5
Bismuth	1.8	1.2

All metals are fusible, but their points of fusion vary very widely as shown in the following table :—

MELTING POINTS OF COMMON METALS.

Metal.	Melts at °C.	Metal.	Melts at °C.
Mercury	−39	Aluminium	750
Potassium	+62	Silver	954
Sodium	97	Gold	1035
Tin	228	Copper	1054
Bismuth	270	Cast iron	1150
Cadmium	315	Wrought iron	1500
Lead	334	Platinum	1780
Zinc	423	Iridium	1950

Metals are in their ordinary condition perfectly opaque to light, but some can be beaten into leaves fine enough to transmit light. In some cases, metals have distinctive colours, as in the case of gold and copper.

The specific gravity of the metals as compared with water varies considerably, lithium being the lightest, whilst osmium, and iridium are the heaviest.

SPECIFIC GRAVITIES OF COMMON METALS.

Lithium	0.59	Cobalt	8.5
Potassium	0.86	Cadmium	8.6
Sodium	0.97	Copper	8.8
Calcium	1.58	Bismuth	9.8
Magnesium	1.75	Silver	10.5
Aluminium	2.56	Lead	11.4
Barium	3.75	Mercury	13.59
Antimony	6.7	Gold	19.3
Zinc	7.1	Platinum	21.5
Tin	7.3	Iridium	22.4
Iron	7.8	Osmium	22.4

Metals may be divided into two groups according to their specific gravities, those below five being called the "light metals," whilst those above are called the "heavy metals." The light metals generally exhibit considerable chemical energy and oxidise readily, forming strong basic oxides, whilst the heavy metals are less energetic and form weaker basic compounds.

The cohesion existing between the particles of metals varies considerably. When hammered some metals can be beaten out into thin leaves and are called "malleable," others crumble up and are called "brittle." If a metal can easily be drawn into wire it is said to be "ductile."

The "tenacity" of a metal is the resistance it offers to being broken by a tensile strain and metals differ considerably in this respect. A wire $\frac{1}{12}$th of an inch in diameter (2m.m.) of the following metals requires the following weights to tear it asunder :—

Nickel ...	750 lb.	Platinum	250 lb.	Zinc ...	50 lb.
Iron ...	500 ,,	Silver ...	170 ,,	Tin ...	32 ,,
Copper ..	274 ,,	Gold ...	136 ,,	Lead ...	24 ,,

The ordinary metals may be divided into five groups according to their affinity for oxygen as shown by their action on water and the action of heat on their oxides.

GROUP I.—Potassium, sodium, barium, strontium, calcium. These are called the metals of the alkalis and alkaline earths; they decompose water at ordinary temperatures, and form oxides which are not broken up by heat.

GROUP II.—Magnesium, aluminium, manganese, iron, chromium, nickel, cobalt, zinc and cadmium. These metals only decompose water at temperatures ranging from 50° C. to red heat. They form oxides not broken up by heat.

GROUP III.—Tin and antimony. They decompose water at a red heat, but will not do so at ordinary temperatures. Their oxides are not broken up by heat alone.

GROUP IV.—Copper and bismuth only decompose water at very high temperatures; and form oxides not decomposed by heat alone.

GROUP V.—Mercury, silver, platinum, and gold. These metals do not decompose water at any temperature, and form oxides which can be decomposed by heat alone.

Potassium and sodium are called the metals of the alkalis, and strongly resemble each other in their properties. Potassium or "kalium" (K=39.1) was not known until 1807, when Sir Humphrey Davy succeeded in breaking up potassic hydrate by a strong galvanic current.

It is a soft white metal which, when cut, shows a silvery surface, which at once tarnishes in contact with air, owing to the formation on it of potassic oxide; when thrown on to water it decomposes it, forming potassic hydrate, and the heat evolved is sufficient to ignite the escaping hydrogen. It fuses easily when heated and is converted into a green vapour; this can best be seen by heating it in a current of hydrogen as, if any air be present, the potassium catches fire and burns with a violet flame, forming potassic oxide (K_2O).

The metal is prepared by heating "cream of tartar" or potassic hydric tartrate, which breaks up, evolves water and carbon dioxide, and leaves behind an intimate mixture of potassic carbonate and finely divided carbon, and on further heating in an iron retort, this breaks up into potassium and carbon monoxide:—

$$\overset{\text{Potassic carbonate}}{K_2CO_3} + \overset{\text{Carbon}}{C_2} = \overset{\text{Carbon monoxide}}{3(CO)} + \overset{\text{Potassium.}}{K_2}.$$

The potassium distils over in the atmosphere of carbon monoxide, and is condensed in flat copper receivers containing mineral oil, which are kept cool by the external application of water. Under certain conditions the potassium in distilling forms an explosive compound with the carbon monoxide.

The most important salt formed by potassium, is potassic nitrate, which has been treated at length under "gunpowder."

The compounds of potassium may be recognised by adding solution of platinic chloride to a strong aqueous solution of the salt, when a yellow crystalline precipitate is obtained on stirring the mixture; and also by the violet colour which they impart to flame when a fragment is taken on a clean platinum wire, moistened with hydrochloric acid, and then heated in the inner blow-pipe flame. Potassium is one of the lightest of the metallic elements, having a specific gravity of 0.865, and an atomic weight of 39.1.

Sodium very strongly resembles potassium, both in the elementary state and in its compounds, but is far more abundant in Nature, common salt or sodic chloride existing in enormous quantities in sea water and also in very extensive deposits found in many parts of the world.

In warm countries sea water is run into shallow tanks, where it evaporates under the heat of the sun and on reaching a specific gravity of 1.2 begins to deposit coarse crystals of crude sodic chloride known as " bay salt," which after being allowed to stand and drain free from the deliquescent magnesic chloride, are ready for use in the manufactures in which it is employed ; whilst the " bittern " or mother liquor which has given birth to the crystals is utilised for the production of bromine.

Sodium like potassium is prepared by distilling the carbonate with finely divided carbon, but in order to prevent the mass fusing a little chalk is added to the mixture. The metal is soft and easily cut with a knife and like potassium must be kept under mineral naphtha, in order to prevent its coming in contact with oxygen, for which it has an enormous affinity. When thrown on water it decomposes it, forming sodic hydrate and evolving hydrogen, but the temperature produced not being so high as in the case of potassium, the gas is not inflamed, unless the metal should be prevented from freely moving over the surface of the water, in which case the temperature rises to the point of ignition.

Sodium has a specific gravity of 0.97 and an atomic weight of 23.

The compounds of sodium are amongst the most important in Nature, sodic chloride being essential to animal life and being also used to a very large extent for glazing earthenware, and for agricultural use, whilst carbonate of soda is of the greatest importance and use in the arts and manufactures, as well as for cleansing purposes.

Up to the year 1790, Europe was almost entirely dependent upon natural sources for sodic carbonate, which was employed as one of the most essential substances in the manufacture of soap and glass. England obtaining her supplies from the ash of seaweeds collected and burnt on the Scotch and Irish coasts and called "kelp," whilst the Continental supply was derived from the ash of certain kinds of marine plants growing on the coast of Spain, which was known as "Barilla."

This ash, however, only contains about one fourth of its weight of sodic carbonate, so that this latter substance was very expensive, and the manufactures of soap and glass, which are dependent upon it, were very much hampered by its cost. During the French Revolution, the price of "barilla" had risen so high, that a premium was offered for the discovery of a cheap method of preparing sodic carbonate, and this led to the discovery by "Leblanc" of a process by which it can be prepared from common salt, a process which, with slight modifications, is in use at the present time.

Common salt (sodic chloride) is mixed with an equal weight of sulphuric acid upon the hearth of a reverberatory furnace, which converts it into sodic sulphate, at the same time expelling hydrochloric acid gas, which, if allowed to escape, would kill all the vegetation in the neighbourhood: the fumes are therefore made to pass up towers filled with coke, down which water is allowed to trickle, and as hydrochloric acid gas is intensely soluble in water, the acid is dissolved and forms the solution which is commercially known as "Muriatic Acid" or spirit of salt.

The dried sodic sulphate called "salt cake" is then mixed with an equal weight of chalk (calcic carbonate) and about one half its weight of fine coal dust, and is again heated upon the hearth of the furnace, when a decomposition takes place: carbon monoxide is evolved and a mixture of sodic carbonate with lime and calcic sulphide is left. This mass is called "black ash," and it is next treated with water, which dissolves out the sodic carbonate, and leaves most of the calcic sulphide behind; the solution then has air blown through it to oxidise any calcic sulphide to sulphate, which being very slightly soluble, settles out, and the clear liquid is then evaporated and yields crystals of impure sodic carbonate called "soda ash."

This contains some sodic sulphate and chloride, and also some caustic soda, and it is purified by mixing it with more fine coal or sawdust, and again heating, when the carbon dioxide produced converts any caustic soda present into sodic carbonate; and on dissolving the mass in water and evaporating, crystals of common washing soda ($Na_2CO_310H_2O$), consisting of sodic carbonate with ten molecules of water of crystallisation, are formed.

The chief reactions taking place during this process may be represented as:—

$$\text{I.}\quad \overset{\text{Sodic chloride}}{2(\mathrm{NaCl})} + \overset{\text{Sulphuric acid.}}{\mathrm{H_2SO_4}} = \overset{\text{Sodic sulphate}}{\mathrm{Na_2SO_4}} + \overset{\text{Hydrochloric acid.}}{2(\mathrm{HCl})}.$$

$$\text{II.}\quad \overset{\text{Sodic sulphate}}{\mathrm{Na_2SO_4}} + \overset{\text{Chalk}}{\mathrm{CaCO_3}} + \overset{\text{Carbon}}{4\mathrm{C}} = \overset{\text{Sodic carbonate}}{\mathrm{Na_2CO_3}}$$

$$+ \overset{\text{Calcic sulphide}}{\mathrm{CaS}} + \overset{\text{Carbon monoxide.}}{4(\mathrm{CO})}.$$

Several other processes have, of late years, come into extensive use, one of the most important being the "ammonia-soda or Solvay's process," which consists of passing carbon dioxide through a saturated brine solution, containing $\frac{1}{5}$th its own volume of strong ammonia solution, when sodic bicarbonate is thrown down:—

$$\overset{\text{Salt}}{\mathrm{NaCl}} + \overset{\text{Ammonic hydrate}}{\mathrm{NH_4HO}} + \overset{\text{Carbon dioxide}}{\mathrm{CO_2}} = \overset{\text{Sodic bicarbonate}}{\mathrm{NaHCO_3}} + \overset{\text{Ammonic chloride.}}{\mathrm{NH_4Cl}},$$

and on strongly heating the bicarbonate it breaks up into the carbonate with evolution of carbon dioxide:—

$$\overset{\text{Sodic bicarbonate}}{2(NaHCO_3)} = \overset{\text{Sodic carbonate}}{Na_2CO_3} + \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Water.}}{H_2O}.$$

The secondary products being recovered and used over again.

In ordinary washing soda, the crystals contain ten molecules of water of crystallisation; but if the solution from which the crystals deposit be kept at a temperature of 30° to 50° C., the crystals will contain seven molecules of water of crystallisation.

The common soda crystals ($Na_2CO_310H_2O$) effloresce in dry air and at a temperature of 50° C. fuse, so that in the tropics, a cargo of soda crystals will often become liquid.

Sodic hydrate (NaHO) which is used for many purposes is made either by decomposing the carbonate with slaked lime (calcic hydrate)—

$$\overset{\text{Sodic carbonate}}{Na_2CO_3} + \overset{\text{Calcic hydrate}}{CaH_2O_2} = \overset{\text{Sodic hydrate}}{2(NaHO)} + \overset{\text{Calcic carbonate.}}{CaCO_3},$$

or by taking the mother liquor, formed in the manufacture of sodic carbonate (by treating the black ash with water, and evaporating and allowing the sodium salts to crystallise out), and after evaporating and oxidising it with sodic nitrate to break up the sulphide, fusing it and casting into moulds.

The salts of sodium give no precipitates with the ordinary reagents, but may be recognised by the intense yellow colour which they impart to flame.

The three remaining metals of the group—barium, strontium and calcium—may be obtained by decomposing the fused chlorides by the galvanic current, or by the action of sodium, but have no practical application in the metallic state.

The salts of barium have but a limited use, the precipitated sulphate being used to a small extent as a pigment under the name of "permanent white," whilst the carbonate is used in making some kinds of glass. Barium salts impart a yellowish-green colour to flame.

Strontium salts are less abundant than the corresponding barium compounds and like them have a very limited use, being chiefly used in the manufacture of coloured fires, strontium compounds giving to flame a magnificent crimson colour.

The compounds of calcium, on the other hand, are universally employed and are of the greatest importance.

Calcium ($Ca = 40$) forms a very large proportion of the Plutonic rocks, of which the earth is composed, and occurs in considerable quantities, forming whole mountain chains of limestone, chalk and gypsum. It is also found in all animals and vegetables, being absorbed by means of their food.

The metal itself is of a light yellow colour, of specific gravity 1.58, is harder than lead, and very malleable. In ordinary air it combines slowly with the oxygen, but at a red heat it fuses and burns with a brilliant light, forming calcium monoxide or lime:—

$$\underset{\text{Calcium}}{Ca} + \underset{\text{Oxygen}}{O} = \underset{\text{Calcium monoxide.}}{CaO.}$$

Calcium occurs principally as the carbonate ($CaCO_3$), and from this all the manufactured compounds of lime are prepared. The forms in which the carbonate are found are very numerous. In the amorphous state it exists as limestone and chalk. The crystalline forms being calc spar or Iceland spar, and arragonite. Marble has also a crystalline form, and sometimes is found coloured or variegated by the presence of oxides of iron and manganese. Black marble owes its colour to the presence of bituminous matter. Calcium carbonate is also the principal constituent of egg shells, the shells of fishes, and coral. All forms of calcium carbonate decompose when heated, splitting up into lime and carbon dioxide gas, *e.g.* :—

$$\underset{\text{Marble}}{CaCO_3} = \underset{\text{Lime}}{CaO} + \underset{\text{Carbon dioxide}}{CO_2}.$$

This process is carried out on an enormous scale for the preparation of calcic oxide or quick lime for manufacturing and building purposes, by heating limestone by means of layers of fuel in a kiln, which consists of a conical brick building. The limestone loses its carbon dioxide and is raked out in the form of burnt or quicklime. This body has the property of absorbing water and forming a hydrate called slaked lime ($Ca(HO)_2$). The reaction takes place with great evolution of heat, the hard stony masses of quicklime swell and crumble to a fine powder. If the limestone contains much silica, alumina or magnesia, the resulting quicklime loses the property of slaking to a considerable extent.

Calcium hydrate is only slightly soluble in cold water (1 part in 700) and still less so in hot water, and the excess precipitates out on boiling. Lime water is very strongly alkaline ; it absorbs carbon dioxide readily, a precipitate of calcium carbonate being deposited. On account of the strong alkalinity of calcium hydrate, and its cheapness, it is extensively used in manufacturing processes. If a stream of carbon dioxide gas be passed through lime water, a precipitate of ($CaCO_3$) is obtained, which, however, redissolves in excess of the gas, forming a double carbonate ($CaCO_3,H_2CO_3$), which is soluble in water. This compound is found in all natural waters coming from chalky districts, and constitutes the so-called temporary hardness of the water. On boiling, the excess of carbon dioxide is driven off and the calcium carbonate precipitated.

Calcium sulphate ($CaSO_4$) occurs in Nature as anhydrite, but more generally combined with two molecules of water, as selenite, alabaster and gypsum ($CaSO_4 2H_2O$). From gypsum, the substance called plaster of Paris is obtained, by heating the former to a temperature between 150° to 200° C., it then loses about two thirds of its water and forms a substance which on being powdered, has the property of recombining with water and forms a hard mass, which expands at the moment of setting or solidifying and is therefore much used in taking casts.

In burning the gypsum to form "plaster of Paris" care has to be taken to avoid too high a temperature, as if it is what is termed "overburnt" it to a great extent loses the property of recombining with water. An addition of a small percentage of lime to plaster of Paris (not more than 10 per cent.) increases the rapidity of setting and makes it harder; this latter property being also induced by addition of a little solution of alum to the plaster and again burning.

Plaster of Paris must always be kept in a dry place and out of contact with moist air, as otherwise it absorbs water, and to a great extent loses its power of setting.

Calcium sulphate is slightly soluble in water (1 part in 400, at 35° C.), and less so in hot water. It is one of the chief causes of the permanent hardness of water, which is not removed by boiling. The presence of other salts, such as sodic and magnesic chlorides, increase its solubility in water.

The salts of calcium impart a yellowish red colour to flame.

The metals of this first group all impart a particular colour to flame, but when two or more are present at the same time the colours often interfere with or mask each other, but their presence is easily detected by spectrum analysis.

When a ray of light passes obliquely from one medium to another, it becomes bent or refracted, and the amount of refraction varies according to the density of the medium. It is for this reason that a stick plunged obliquely into water appears bent, the immersed part appearing raised. Now ordinary sunlight consists of a number of beams or rays of various colours which blend together and form white light, and these rays differ in their refrangibility or bending power.

If a beam of white light be allowed to fall on the face of a wedge shaped piece of glass, termed a prism, it will be found that after passing through the glass, it has been broken up into an oblong band, possessing all the tints of the rainbow, which is called the solar spectrum. This spectrum contains an infinite number of different tints, which merge one into the other, but it will be easy to distinguish seven principal colours arranged in the following order; violet, indigo, blue, green, yellow, orange, red, the violet being the most refrangible, and the red least.

Within the last twenty-five years Bunsen and Kirchhoff have, by means of an instrument called the Spectroscope, utilised this phenomenon to found the study of spectrum analysis. In the spectroscope a ray of light is projected (through a narrow vertical slit placed in the focus of a lens) on to a prism, and the refracted light is examined by means of a telescope. A scale is also provided in the instrument so as to divide off the different parts of the spectrum.

Not only white light, but most coloured light, is found to consist of rays of different refrangibility, and if an incandescent solid or liquid be examined, it will be found to give a continuous spectrum. If, however, an incandescent gas be examined, it will be found that the light emitted gives bright bands separated by dark intervals. The position of these bright bands varies for every element; but for the same element, under similar conditions, the position is definite, so that it can be recognised by simply studying the position the bands occupy.

Certain chemical substances, especially the salts of the alkalis and alkaline earths, when heated in a non-luminous flame, impart a characteristic colour to that flame, and the presence of the substance may be determined by that colour. On examining such a flame by means of the spectroscope, the detection can be made with still greater certainty and delicacy. Sodium and sodium salts impart a yellow colour to the flame, and if this be examined it will be found that the spectrum consists of two fine bright yellow lines very close together, whilst the purple potash flame gives a spectrum in which there are two bright lines—one in the extreme end of the red, and the other in the violet. If a flame tinted by a mixture of sodium and potassium salt be examined by the naked eye, the sodium will mask the colour of the potassium, whilst examination by the spectroscope shows the yellow bands due to the sodium in the proper position, and the potassium lines are as plainly seen as they would have been had no sodium been present. By this method less than $\frac{1}{180000000}$th part of a grain of sodium can be detected.

If a ray of sunlight be allowed to fall upon the slit of a spectroscope, it will be found to give a spectrum, intersected by a number of fine dark lines, some of which are more prominent than others. These lines always occupy the same relative position in the solar spectrum, and are termed "Fraunhofer's lines," after a German optician, who first satisfactorily mapped and described them. If the position of these dark lines be compared with bright lines in the spectra given by certain metals, such as iron, magnesium, sodium, &c., it is seen that each of the bright lines of the particular metal coincides, not only in position, but also in breadth and intensity, with a dark solar line. The question at once arises, are these coincidences due to the presence of these metals in the sun? And if this is the case, why do the lines in the solar spectrum appear dark? This can be easily explained.

We have seen that a sodium coloured flame gives a double band of bright yellow light when viewed through the spectroscope. Now, if a bright white light is placed behind the sodium coloured flame so that the light passes through and on to the slit, a continuous spectrum is seen, but there will be a double black band now where the yellow one was before, the yellow flame of the sodium having absorbed the yellow light in that particular part. The existence of the dark lines in the solar spectrum is probably due to passage of white light through the vapour of the metals in question, present in the atmosphere of the sun, and these vapours absorb exactly the same kind of light which they are able to emit. An accurate comparison of the Fraunhofer lines with the bright lines of the various elements has revealed the fact that iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc and hydrogen are present in the sun's atmosphere. The light from the fixed stars has also been investigated, and these appear to possess a constitution similar to that of the sun. The spectra of nebulæ, however, only show bright lines; hence, these consist of uncondensed, incandescent masses of vapour.

Solutions of coloured salts, and many coloured media absorb light of different refrangibility, and accordingly, when interposed between a source of white light, such as an ordinary gas flame or Argand burner and the slit of the spectroscope, give a spectrum which is marked by bands or dark lines; these are termed absorption spectra, and may be made use of in detecting certain substances. Not only coloured solutions, but water, ammonia solution and many colourless substances, will give absorption spectra if about 6 to 8 ft. of the liquid be looked through.

CHAPTER XXII.

THE METALS (*continued*).

Magnesium and its uses—Aluminium—Aluminium bronze—Alum—Manganese—Chromium—Oxides of chromium—Cobalt—Nickel—Iron—Ores of iron—Calcining iron ore—The blast furnace—Pig iron—Varieties of cast iron—Wrought iron—Puddling process—Bessemer process for converting cast into wrought iron—Steel—Cementation process—Bessemer process—Siemens-Martin process—Cast steel—Krupp's cast steel—Compressed steel—Armour plates—Manganese steel—Nickel steel—Zinc—Galvanised iron—Cadmium.

MAGNESIUM (Mg=24) occurs widely diffused in Nature and in large quantities, especially as carbonate in dolomite and magnesite, as sulphate in Epsom salts, and as silicate in asbestos, meerschaum, talc, &c. It is found as sulphate and chloride, in sea water.

Magnesium has only been extracted in any quantity during the last few years, a considerable demand for it having arisen in consequence of its property of burning in air with a very brilliant flame, rich in actinic or chemical rays, which make it valuable as a source of artificial light in photography. A wire of 0.33 millimeter in diameter in burning produces a light equal to that of 74 standard candles. When magnesium burns in air or oxygen, the oxide (MgO) is formed, a white powder, slightly soluble in water, giving a feeble alkaline reaction, and much used in pharmacy.

Magnesium dissolves up readily in acids to form the different salts, which are in the case of the nitrate, chloride and sulphate very soluble in water. The carbonate which also occurs native, is prepared by precipitation from a soluble magnesium salt by means of sodium carbonate, and constitutes the "*magnesia alba*" of pharmacy. Magnesium salts are completely precipitated by means of ordinary sodic phosphate, in the presence of ammonium chloride and free ammonia, which throws down ammonio-magnesium phosphate, having the formula ($MgNH_4 PO_4, 6H_2O$).

All magnesium salts act more or less as purgatives.

Aluminium ($Al = 27.5$), is one of the most abundant elements, but is never found in the free state; it occurs chiefly as silicate and oxide as in felspar, and all the older rocks, also in clay, marl, and slate.

Aluminium is a white metal, with a tinge of blue, is very ductile and malleable, and possesses a bright metallic lustre that does not tarnish in air at ordinary temperatures.

Aluminium is the lightest of those metals which are sufficiently permanent in air to allow of their use, and for this reason is employed for purposes for which lightness and tenacity are of value, as in beams of delicate balances, optical instruments, &c. The metal itself is extremely sonorous when lightly struck.

Several useful alloys are obtained with this metal. Aluminium bronze is an alloy containing 90 parts of aluminium and 10 parts of copper; it has the colour of gold, and has twice the tenacity of gunmetal. Aluminium forms but one compound with oxygen, called alumina (Al_2O_3). In the natural crystallised state it constitutes, according to its colour, various precious stones, such as the sapphire, ruby, amethyst, corundum and emery. Combined with silica and silicates of various metals it forms the garnet, emerald, topaz, beryl, and the splendid blue mineral known as lapis lazuli. Alumina combined with silica forms clay.

One of the most important classes of salts of this metal is the alums. These consist of double sulphates of triad metals such as aluminium with the sulphates of the monads. For instance, potash alum has the formula ($Al_2 3(SO_4) K_2SO_4 24H_2O$), and can be formed by mixing, in proper proportions, solutions of sulphate of alumina and sulphate of potassium, and crystallising.

Very frequently ammonic sulphate (from gas liquor) is used instead of the potassium salt, in which case ammonia alum is formed $(NH_4)_2SO_4$, $Al_2 3(SO_4) 24H_2O$.

Alum is a white crystalline body, soluble in water, and has an astringent taste. Its solution has an acid reaction. It is largely used as a mordant to fix colouring matters on calico, the aluminic hydrate combining with certain organic colouring matters to form insoluble "lakes." The metal itself is prepared by heating the double chloride or double fluoride of aluminium and sodium, with metallic sodium, in a crucible or on the hearth of a reverberatory furnace. The production of the metal and its use has been limited owing to the high price of the metallic sodium necessary to produce it. This difficulty has now been partly overcome, and we may expect to see aluminium in more general use. The metal is soluble in hydrochloric and sulphuric acids with evolution of hydrogen, but is not acted on by nitric acid; it is rapidly attacked by caustic alkalis with the evolution of hydrogen.

The two next metals of this group—manganese and chromium—have not by themselves received any useful application, although when alloyed with iron they give it certain properties which will be considered when studying the latter element.

Manganese ($Mn=55$) occurs chiefly combined with oxygen as pyrolusite or dioxide (MnO_2); also as manganese spar or carbonate ($MnCO_3$), or Braunite (Mn_2O_3) and Hausmannite (Mn_3O_4).

Manganese is a reddish grey metal, very hard and brittle, scratching glass; but, owing to its rapidly oxidising in moist air, has to be kept under naphtha. The metal combines with oxygen, forming a very complete series of oxides; the lowest being basic and the highest acid forming, whilst the intermediate ones are neutral.

The most important oxide is the dioxide (MnO_2). This is found tolerably pure, and is largely used in the preparation of chlorine gas (*see* Chlorine). The oxide is a powerful oxidising agent in the presence of sulphuric acid; *e.g.*, oxalic acid is completely oxidised by this mixture to carbon dioxide.

$$\overset{\text{Manganese dioxide}}{MnO_2} + \overset{\text{Sulphuric acid}}{H_2SO_4} + \overset{\text{Oxalic acid}}{H_2C_2O_4} = \overset{\text{Manganese sulphate}}{MnSO_4}$$

$$+ \overset{\text{Carbon dioxide}}{2(CO_2)} + \overset{\text{Water.}}{2(H_2O)}.$$

Manganous oxide (MnO) is a strong base, and dissolves in acids to form pink or white salts in which the manganese is a dyad.

If a salt of manganese be fused with potassic nitrate and caustic potash, a dark green amorphous mass is obtained, which consists of manganate of potash (K_2MnO_4). This dissolves readily in water, forming a green solution (Chameleon liquor), which rapidly changes to a pink colour on the addition of acid. This change is best effected by passing a stream of carbon dioxide gas through a solution of the manganate, when the permanganate is formed ($KMnO_4$), known as Condy's fluid. This substance is largely used as a disinfectant owing to its power of oxidising organic matter.

Chromium ($Cr=52.4$) is found as a constituent of many minerals, and always acts as a colouring agent when present. The metal is of a steel grey colour, very hard and brittle and melts at a higher temperature than platinum.

Chromium forms several oxides. The chromic oxide

(Cr_2O_3) is the most important and is used as a green pigment. If this oxide be fused with potash, and some oxidising agent, such as potassic nitrate, a yellow salt is obtained consisting of potassic chromate (K_2CrO_4). If sulphuric acid be added to this salt in sufficient quantity to neutralise half the potassium and the solution allowed to crystallise, potassium bichromate is formed ($K_2Cr_2O_7$). This salt acts as a strong oxidising agent and is used in photography and in calico printing.

Cobalt (Co=59) occurs in the metallic state in meteoric iron, also is found combined with arsenic as Speiss cobalt ($CoAs_2$) and cobalt glance (CoAsS). This metal resembles iron in colour, but melts at a somewhat lower temperature, and has nearly double the tenacity of iron. It is only slightly malleable but is very ductile. It is not acted on by dry air, but oxidises rapidly at a red heat. The metal dissolves in acids to form cobaltous salts, which are soluble in water, forming red solutions.

$$\underset{\text{Cobalt}}{Co} + \underset{\text{Hydrochloric acid}}{2(HCl)} = \underset{\text{Cobalt chloride}}{CoCl_2} + \underset{\text{Hydrogen.}}{H_2}.$$

This salt crystallises in dark red prisms with six molecules of water ($CoCl_26H_2O$) which lose part of their water when heated to 120° and become blue ($CoCl_22H_2O$), becoming anhydrous at 140°. By writing with a dilute solution of cobaltous chloride on paper, the writing after drying at ordinary temperature becomes almost totally invisible; on warming the paper the writing becomes dark blue, but fades away on cooling in moist air (sympathetic ink).

Cobalt forms several oxides, but only the cobaltous oxide (CoO), in which the metal is a dyad, yields stable salts. This oxide is extensively used to impart a blue colour to glass. Fused with an acid silicate and ground to a powder it forms the pigment smalt. The blue colour is not affected by acids or alkalis.

Nickel (Ni=59) is found more extensively than cobalt, chiefly as the arsenide (NiAs); and is also found in meteoric iron. Nickel is a whitish metal, and takes a high polish, which is permanent in dry, and nearly so in moist air. It is malleable, ductile, and of great tenacity. The metal is used chiefly alloyed with zinc and copper to form the compound called German silver, also extensively as a coating on other metals, called nickel plating, the metal being precipitated from a solution of the double cyanide, by means of the galvanic current. The metal dissolves rapidly in acids to form salts in which the metal is a dyad, the hydrated salts being green, and the anhydrous yellow.

Both nickel and cobalt, when fused with iron, give an alloy which is very hard, and resists to a considerable extent the corrosive action of acids. Kreuss has lately isolated a substance from these two metals which appears to be common to both, to which he has given the name "Gnomium."

Iron (Fe=56) is the most important as well as one of the most abundant of the metallic elements, its compounds existing in every part of the globe, whilst it plays an important part in animal and most vegetable organisms.

Metallic iron is met with in small quantities in meteorites, metallic masses which occasionally fall upon the earth from unknown sources, and which generally contain small quantities of other metals, such as nickel, cobalt, chromium, &c.

The chief native compounds which are sufficiently abundant to make them valuable as a source of the metal are—

		Percentage of iron in pure ore.
Magnetic iron ore	Fe_3O_4	72
Specular iron ore	Fe_2O_3	70
Red hæmatite		
Brown hæmatite	$2(Fe_2O_3)3(H_2O)$	60
Spathic iron ore	$FeCO_3$	48
Clay ironstone	$FeCO_3$ mixed with clay	17 to 48
Iron pyrites	FeS_2	46

And these ores all contain certain quantities of foreign impurities, some of which, like sulphur and phosphorus, are nearly always present and exert a deleterious influence on the metal obtained from them. The magnetic iron ore, specular ore and red hæmatite are the purest ores, and it is from these, therefore, that the best iron is obtained, whilst the difficulty in separating the sulphur prevents iron pyrites from being used as a source of the metal.

Magnetic and specular iron ore, however, do not exist in sufficiently large quantities in England for them to be much used and the density of the red hæmatite offers considerable obstacles to its easy reduction, so that the most commonly used ores in this country are the brown hæmatite, the spathic iron ore and the clay ironstone, and in spite of the low percentage of metal present in the latter ore, it is the one from which by far the largest proportion of iron is made in England.

In using spathic iron ore or clay ironstone the ore has to undergo a preliminary process of roasting which decomposes the ferrous carbonate and drives off carbon dioxide, leaving the iron as oxide :—

$$\begin{array}{ccccccc} \text{Ferrous carbonate} & & \text{Oxygen} & & \text{Carbon dioxide} & & \text{Ferric oxide.} \\ 4(FeCO_3) & + & O_2 & = & 4(CO_2) & + & 2(Fe_2O_3). \end{array}$$

This calcination not only increases the percentage of iron present in any weight of the ore, but also the escape of the carbon dioxide leaves the roasted ore in a porous condition which is highly advantageous in the further processes of smelting, and the ferrous oxide becomes converted into ferric oxide by the oxygen of the air present.

Calcining the ore used to be carried out by mixing it with small coal, making the mixture into long heaps and igniting them at the end nearest the quarter from which the wind was blowing, when the burning coal roasted the ore, in the same way that in a "ballast" heap the small coal or "slack" employed bakes the clay to "ballast."

This method, however, does not give reliable results as when the wind is high, the heap burns too fiercely and some of the ore passes into a semi fused condition, whilst under other circumstances and in other parts of the heap the ore is not sufficiently calcined, so that it is now more usual to roast the ore with small coal in kilns or "calciners," which give much more uniform results and the roasted ore is drawn from the kiln into iron barrows and removed to the blast furnace, whilst still hot, so avoiding the expenditure of more heat than is necessary.

When hæmatite ore is used, this preliminary operation is not gone through as the iron is already in the form of ferric oxide, and is fit for using at once in the blast furnace, which consists of a cylindrical furnace often as much as sixty feet in height, built of masonry, bound together by iron plates and lined inside with firebrick and tapering into a cone at the top and also towards the bottom (Fig. 53).

The top of the furnace is closed by an inverted cone (C) kept in position by a balanced lever arm, which although it will allow of fuel and ore being fed into the furnace, yet prevents the escape of the gases generated during the smelting, these being led away by the side tube (D), and being combustible, are utilised for heating a blast of air which is forced in through the "twyer" pipes (B) at the bottom of the furnace under a pressure of several pounds on the square inch and so produces a strong up draught.

Into this furnace enough coke is first put to fill the lower portion, and above this the calcined ore mixed with limestone is arranged in layers with coke between them until the furnace is full. The coke at the bottom of the furnace is now ignited and caused to burn fiercely by the blast of air blown into the bottom of the furnace.

The ore and other materials present in the furnace (A) are first thoroughly dried by the uprush of heated gases, and as soon as the temperature has risen to a sufficient degree the chemical changes commence.

At the bottom of the furnace the coke burns in the hot blast with formation of carbon dioxide :—

Carbon (coke)		Oxygen (in air)		Carbon dioxide.
C	$+$	O_2	$=$	CO_2,

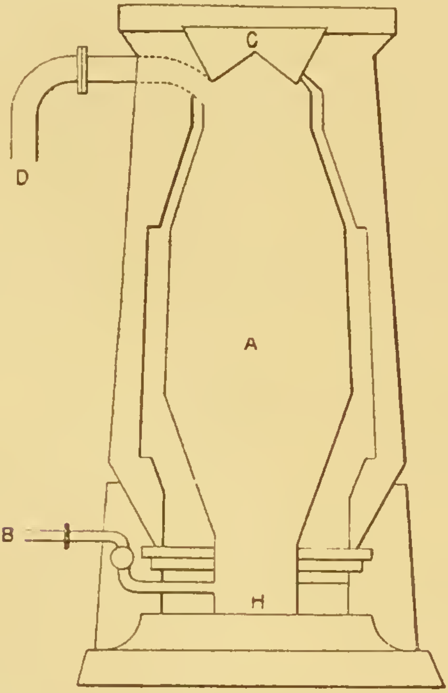

Fig. 53.

and this passing over the mass of heated coke above it is converted into double the volume of carbon monoxide :—

Carbon dioxide		Carbon		Carbon monoxide.
CO_2	$+$	C	$=$	$2(CO)$,

and the hot carbon monoxide then coming in contact with the layer of heated ore above it reduces the ferric oxide to iron, once more being itself brought back to the condition of carbon dioxide :—

$$\overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Carbon monoxide}}{3(CO)} = \overset{\text{Iron}}{Fe_2} + \overset{\text{Carbon dioxide.}}{3(CO_2)},$$

and the carbon dioxide is again reduced to carbon monoxide in the next layer of coke, and this again performs its function of taking oxygen from more ferric oxide, the alternate oxidation at the expense of the ore and reduction by more hot carbon continuing, until a portion of the furnace too cool to carry on the action is reached.

The iron so formed, together with some lower oxide of iron, is scattered in small particles throughout the clay (silicate of alumina) originally present in the ore, and the iron is so infusible that it is impossible to separate it without heating the mass to a temperature at which the clay would fuse, and if this were done, the lower oxide of iron present would combine with the clay and other siliceous matters to form a fusible slag, which would waste a large proportion of the iron; and it is to prevent this that the limestone is added. The limestone burns to lime, which readily unites with the clay to form an easily fusible double silicate of lime and alumina, which runs down and collects in the lower portion of the furnace, whilst the iron and oxide of iron being reduced to the metallic form, gradually combine with some of the carbon present, and also take up a little silicon, phosphorus and sulphur, melting and running down into the bottom of the furnace, being protected from the oxidising action of the blast at the bottom of the furnace by the coating of slag which envelops each particle of iron. The molten slag and metal having reached the bottom of the furnace, run into a cavity called the crucible (H), made to receive them, and there (being specifically heavier than the molten slag) the metal sinks through it and forms a layer at the bottom; and when sufficient of this has collected, the crucible is tapped and the metal is run out and cast into masses called "pigs." This "cast" or "pig" iron is classified into grey iron and white iron, according to the appearance presented by its surface when freshly fractured, and this is dependent upon the state in which the carbon is present in the iron: if it exists mainly in the free state as graphite, the iron is grey and has a coarse grained structure; whilst if the carbon is chiefly in chemical combination, the colour of the iron approaches more nearly to white, and the fracture is more crystalline.

When iron is fused in contact with carbon it can be made to take up nearly 6 per cent. of it, forming a compound approximating to the composition (Fe_4C), and if on cooling the carbon is all retained, it forms a white and very brittle compound, but under certain conditions as the compound cools, a portion of the carbon separates and remains mixed throughout the mass of metal in fine graphite-like crystals, which give the metal a grey fracture. Between the two extremes of grey and white pig iron there are six grades of pig, in which the amount of carbon free and in combination undergoes gradual variation, and which are known in the market by certain numbers, No. 1 being grey and No. 8 white, the intermediate kinds being sometimes known as mottled iron.

The properties of these varieties of cast iron vary very considerably, as also does their composition, as may be seen from the following Table*:—

	Grey.	Mottled.	White.
Iron	90.24	89.31	89.86
Combined carbon	1.02	1.79	2.46
Free carbon	2.64	1.11	0.87
Silicon	3.06	2.17	1.12
Sulphur	1.14	1.48	2.52
Phosphorus	0.93	1.17	0.91
Manganese	0.83	1.60	2.72
	99.86	98.63	100.46

---

* *Bloxam.*

The formation of grey and white pig iron, is, to a great extent influenced by the conditions existing in the furnace; if the conditions be good and fuel plentiful then grey iron is produced, whilst if the supply of coke is scanty, then white iron results.

The differences existing between grey and white pig iron are very marked.

Grey cast iron is comparatively soft and can be easily worked; it has a higher fusing point than white iron, but when fused is more liquid and when used for castings expands at the moment of solidification.

White iron has a higher specific gravity than the grey and is excessively hard and brittle, it fuses at a lower temperature than the grey iron but is never so liquid or so well adapted for taking castings as the grey.

If molten grey iron is suddenly cooled, the graphite which has redissolved in the liquid metal has not time to separate, and the casting becomes in consequence extremely hard and of the appearance of white iron. This is taken advantage of in "chill casting," by which shot and shell cast from grey iron have the apex and outer skin of metal made as hard as steel by casting them in iron moulds.

The large quantities of foreign matter present in cast iron, diminish its toughness and tensile strength, and render it unfit for use in many applications of the metal, and in order to give it the property of toughness, it is converted into a purified form called "wrought iron."

Wrought iron is the purest form of iron used commercially. It is prepared from cast iron by removing the impurities with which the latter is associated, such as carbon, silicon, phosphorus, &c. This purification is based on the fact that when cast iron is heated in contact with oxide of iron, the carbon and silicon combine with the oxygen of the oxide of iron, carbon monoxide being evolved as a gas, and the silicon combines with the oxygen to form silica, which unites with another part of the oxide of iron to form a slag, which is very fusible, and can be easily separated from the metal. The process by which this is effected is called "puddling." A more modern method is called "bessemerising" the metal, in which the impurities are oxidised by blowing fine streams of air through the molten metal. If pig iron is very impure, a preliminary purification is made in a refinery or bloomery.

This consists in fusing the metal and exposing it to the action of a blast of air, in which part of the oxygen has been converted into carbonic oxide by passing it over red hot charcoal or coke. The refinery furnace consists of a shallow rectangular trough, with double walls of cast iron, which are prevented from fusing by the circulation of cold water between them. The trough is sometimes lined with fireclay, and on each side are arranged twyer pipes for the supply of air, inclined to the bottom of the furnace at an angle of 20° to 25°. When the furnace is ready, coke is thrown on to the hearth, and on it pieces of the pig iron are piled which are covered with more coke, and a blast of air is forced in through the twyers. The metal slowly melts, and as it drops down to the bottom of the hearth comes into direct contact with the air from the blast, the result being that part of the silicon is oxidised to silica, carbon to carbon dioxide, and iron to oxide of iron. When all the metal is melted the blast is still allowed to play on the surface of the metal for some time, to further oxidise the mass, bubbles of carbon monoxide rapidly rise to the surface, the molten mass appearing to boil. The metal is removed and run into cast iron moulds kept cool by the circulation of cold water round them. This rapidly cools the molten metal and renders it brittle. The purification of the iron cannot be carried beyond a certain limit in this furnace, as the process is dependent on keeping the iron in a fluid state ; but as the iron is deprived of impurities so it passes from the fluid condition and becomes pasty, and requires to undergo a kneading process in order to bring the impurities into close contact with the oxide of iron.

This is accomplished in the puddling process, which is carried out in a reverberatory furnace. The hearth is composed of firebrick, or of cast iron plates covered with a very infusible layer of slag, and these are kept cool by the circulation of a draught of air. The grate is separated from the hearth by means of firebricks, and thus prevents actual contact of the fuel and the iron to be operated on. This is essential on account of the avidity with which the iron takes up sulphur and other impurities which generally exist in the coal. The oxidised products of combustion come in contact with the iron, and these have not the same bad effect (Fig. 54).

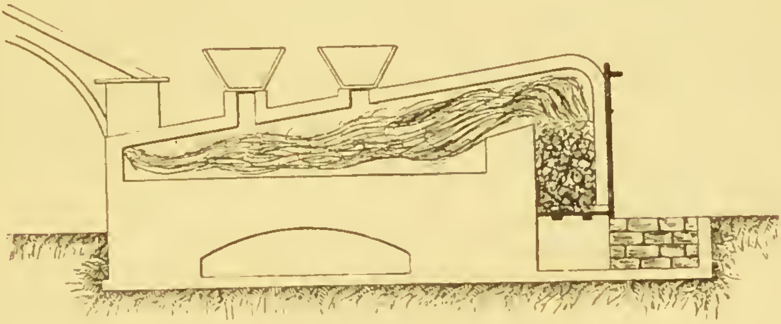

Fig. 54.

A charge of metal together with basic silicate of iron, called "hammer slag," is thrown into the furnace, and the mixture heated. The metal gradually melts down, and the whole mass is well stirred or puddled. In a short time violent action commences, bubbles of carbon monoxide are rapidly formed, and burn at the surface of the metal in small blue jets. The mass gradually loses its fluidity and when the carbon has been reduced to about 1 per cent. becomes pasty. The temperature is now raised, and the mass vigorously worked and broken up. The greater part of the carbon remaining is now removed, and finally the phosphorus. At this stage, the metal having been worked up into balls, is placed under the hammer, which squeezes out any slag, and consolidates the spongy mass of metal into slabs or blooms, which are then passed through rolling machines and converted into bars. These constitute the "rough" or No. 1 bar, and are far from being homogeneous, the metal being hard, but at the same time very brittle. To obtain the "merchant" or No. 2 bar, the No. 1 bar is cut up into short lengths, the pieces are piled, or made up into bundles, which are reheated in a mill furnace and again rolled until the bar is reduced to the required dimensions. If this operation is repeated one or more times, No. 3 bar or the "best iron" is obtained. These repeated rollings squeeze out any slag left in the iron, and render it more homogeneous, and by increasing the fibrous structure of the metal give it great tensile strength.

The great manual labour and exhaustive work involved in the puddling process has led to several methods being tried, the most important of which is that proposed by Bessemer. This consists of running cast iron, which has been melted in a separate furnace, into a Bessemer's Converter (Fig. 55), which takes the form of a cylindrical crucible of wrought iron, lined with a siliceous coating called "ganister," and movable on trunnions. At the bottom of the converter are arranged twyers, and air is conveyed to these through one arm of the trunnion, which is hollow, and which is connected with the blast main. The molten cast iron is ladled into the heated converter, the blast having been previously turned on to prevent the choking of the air tubes. The air bubbles through the molten mixture and combines first with the silicon and the manganese, and then with the carbon. During this process so much heat is given out by the oxidation of these substances as not only to prevent the temperature falling, but in fact to raise it so much as to keep the molten mass liquid (instead of becoming pasty, as in the puddling process), thus enabling the metal to be poured out of the converter at the end of the operation. Owing to the acid properties of the ganister linings of the converter, phosphorus is not removed to any appreciable extent, and consequently pig iron free from phosphorus is used. An improvement has lately been made in substituting a "basic" lining to the furnace, consisting of bricks made by calcining a mixture of ground magnesium limestone and pitch.

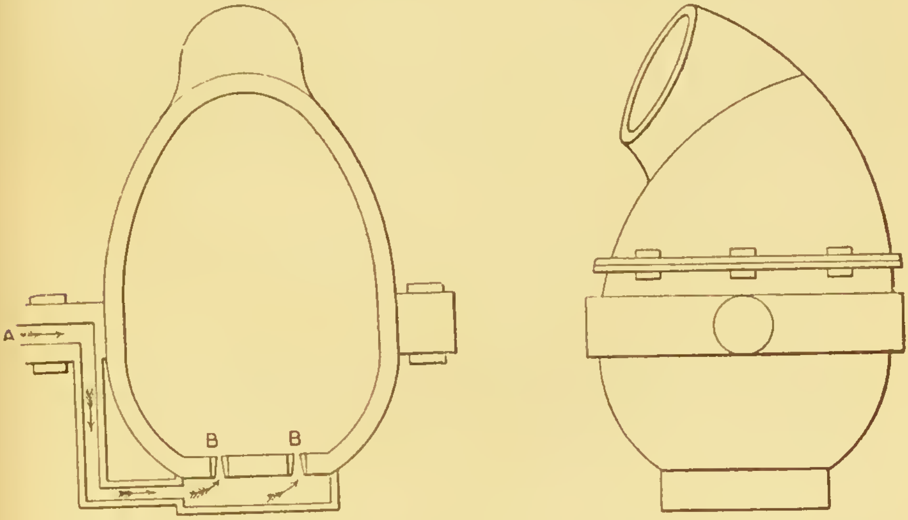

Fig. 55.

By adopting this lining the phosphorus is eliminated in the "after blow," *i.e.*, the blast driven through after all the carbon is burnt out. This process is not, however, extensively used for the production of wrought iron.

Danks's rotating puddling furnace and Crampton's furnace are simply modifications of the above methods. Wrought or bar iron is the purest form of commercial iron, but still contains small quantities of carbon, silicon, sulphur and phosphorus. The small quantity of carbon present (from 0.1 to 0.2 per cent.), increases the hardness and tenacity. The presence of sulphur and phosphorus, however, produces deleterious effects and renders the iron liable to the defects known as red shortness and cold shortness, *i.e.*, the iron is brittle at a red heat if it contain sulphur and at ordinary temperatures if it contain phosphorus. Wrought iron, if fractured, exhibits a fibrous structure, and this seems to account for its superiority in strength over the crystalline forms; in fact, wrought iron under certain conditions, such as constant vibration, has been known to lose its fibrous condition and become crystalline in structure, when it at once becomes brittle. Another feature of wrought iron which distinguishes it from steel is the property of being welded. Two clean surfaces of the metal uniting into a solid piece, when hammered together at a red heat, a property that atones for the infusibility of the wrought iron.

STEEL.

Steel occupies an intermediate position, containing more carbon than wrought, and less than cast iron. It possesses the property of becoming much harder than either, if after being heated to redness, it be suddenly cooled by being plunged into water. The hardest steel contains about 1.2 per cent. of carbon, and can be made from wrought iron by adding 1 per cent. of carbon to it, or from cast iron by stopping the purification at a certain point.

Formerly, steel was principally made by the cementation process which consists of packing bars of wrought iron in an iron box with layers of powdered charcoal, and heating the whole up to a temperature of about 1,000° C., which is maintained for a week to a fortnight, according to the quality of steel required. The box is allowed to cool gradually and the bars, when examined, will be found covered with blisters, due to the liberation of gases from the interior of the bar. It is probable that part of the carbon combines with any oxygen present to form carbon dioxide; and that the iron at a high temperature, decomposes this gas, retains the carbon, and liberates carbon monoxide, which, escaping from the iron produces the blistered surface. In order to render the metal homogeneous, it is cut up into short lengths, the pieces are piled together, and hammered together at a red heat. This forms the "shear steel" used in the manufacture of shears and other tools.

If the blistered steel be fused in a plumbago crucible, a denser and harder variety is obtained, called "cast steel." In order to harden steel, it is only necessary to heat it to redness and suddenly cool by plunging it into water, oil or mercury. In the manufacture of some instruments, however, the steel is too brittle to be of use, and requires to be tempered, which reduces the brittleness at the expense of its hardness. This is accomplished by reheating the hardened steel to different temperatures and allowing it to cool slowly. The more elastic the steel is to be, the higher must be the temperature. The temperature is gauged by the colour of the film of oxide that forms on the surface of the steel at the different temperatures. The following table shows the tempering heats for various implements:—

Temperature.	Colour.	Implements thus tempered.
220° C.	Pale yellow ...	Surgical instruments, razors. &c.
245° C.	Straw yellow ...	Wood cutting tools, dies, &c.
255° C.	Dark yellow ...	Chisels, shears, &c.
265° C.	Brown	Axes, clasp knives, &c.
275° C.	Purple	Table knives
295°–320°C. ...	Blue...	Saws, watch springs, sword blades, &c.

If any of these tempered steels be heated to redness, they are converted into soft steel and at once lose their hardness.

Hard and soft steel seem to bear the same relationship to each other that grey cast iron does to white cast iron, namely: the carbon being in combination with the iron in hard steel, and only mechanically mixed with the iron in the soft steel.

Of late years, much of the steel used is made by Bessemer's improved process, which consists of first preparing a pure iron, by the method described (page 378), and then adding to the molten mass in the converter, the requisite amount of carbon combined in the form of spiegeleisen. This substance is prepared by smelting spathic iron ore, rich in manganese, with charcoal. The introduction of the spiegeleisen causes a violent reaction within the converter, and the formation of a large jet of flame at the mouth. After all action has finished, the molten mass is allowed to stand for a few minutes, and then poured from the mouth of the vessel into the ladle, and direct into the moulds. The whole process only occupies about twenty minutes, and the saving of time as compared with the old cementation process, is enormous.

Siemens-Martin process consists in melting wrought iron or scrap steel, and hæmatite iron ore, in a bath of molten pig iron. This is done on the hearth of a gas furnace. The necessary temperature being obtained by utilising the escaping products, to heat up the gas and air used in the combustion. The metal can be easily tested, and any additions of pig iron or iron ore be made according to requirements.

When the mixture is completely fused, about one per cent. of spiegeleisen and three per cent. of ferro-manganese is added and stirred in, the steel being then tapped and run off into ladles.

Krupp's cast steel, made at Essen, near Cologne, and used for ordnance, shells, &c., is made by smelting hæmatite and spathic ore with coke, in a puddling furnace. The metal before being cast is fused in blacklead crucibles holding from 30 to 40 lb. each.

Sir Joseph Whitworth's compressed steel is obtained by subjecting the molten steel to a pressure varying from 6 to 20 tons on the square inch, the pressure being maintained during solidification of the metal; this causes a shortening of the ingot and also a rise in the specific gravity and produces a superior metal which is much used in the manufacture of ordnance, steel shafting, etc.

The compound plates for armour are made by taking a backing plate of wrought iron containing about 0.04 per cent. of carbon, and a steel facing plate containing about 0.5 per cent. of carbon, and connecting these by distance pieces and screws, so as to leave a space between them, which varies according to the thickness required in the finished plate; these are then heated to redness and placed on end in a rectangular moulding box, and molten steel from a Siemens furnace is run in between them at a temperature which fuses the whole into a solid mass, so that when it is cooled down to redness, it can be withdrawn from the moulding box as a solid plate and is then rolled down to the required dimensions, the hard steel face, the mild steel centre, and the soft iron back being completely united.

The advantages of these compound plates are that the hard steel resists the penetration of a projectile, whilst the mild steel and soft iron prevent the hard steel from shattering under the blow.

Mild steel is steel containing a low percentage of carbon and approaching more nearly to wrought iron in composition, over which, however, for structural purposes it has several advantages, having a greater tensile strength, more elasticity, ductility, and generally greater power of endurance, whilst plates, etc., can be made much larger than is possible with iron.

Manganese is nearly always present in steel, and varies in quantity from 0.25 to 1 per cent., and acts like the carbon in increasing elasticity and tensile strength, but at the same time hardens it and diminishes its ductility. The presence of traces of phosphorus in steel render the metal "cold short," whilst many soft steels are "red short" from the presence of sulphur, and this is, to a certain extent, overcome by the presence of a small quantity (0.5 per cent.) of manganese, which improves the working qualities of the metal.

When the percentage of manganese in a cast steel is increased, the metal rapidly becomes harder and more brittle, until between the limits of 2.5 and 7.5 per cent. the metal is more like glass than steel, and can be reduced to fine powder by a hand hammer. When the manganese rises above 7.5 per cent. this extreme brittleness disappears, and the alloy becomes hard and tough; and it seems probable that "manganese steel" containing about 14 per cent. manganese will prove to be a very valuable alloy for many purposes.

A very remarkable increase in the tensile strength and elasticity of steel is obtained by alloying it with 5 or 6 per cent. of nickel, whilst a larger addition (25 per cent.) seems to prevent corrosion of the metal, which would render the alloy of great value for ship's bottoms; the prohibitive price of nickel, however, renders this application at present impossible.

Iron forms three well defined oxides:—

Ferrous oxide (FeO).
Ferric oxide (Fe_2O_3).
Ferroso-ferric oxide (Fe_3O_4).

Only the first two, however, form salts. Ferrous oxide is very unstable, and has an intense affinity for oxygen, becoming converted into ferric oxide. It can, however, be prepared by passing hydrogen over finely divided ferric oxide heated to a temperature of 300° C. A black powder is formed which catches fire spontaneously in air.

The ferrous salts are more stable, but even these have a great tendency to become ferric salts.

Ferrous sulphate is formed by dissolving iron in sulphuric acid; hydrogen is evolved and a green salt crystallises out containing seven molecules of water ($FeSO_4,7H_2O$). On heating to 280° the water is driven off; and if the salt be heated more strongly, Nordhausen sulphuric acid distils over and ferric oxide is left behind.

Ferrous chloride ($FeCl_2$) can be prepared by the action of iron on hydrochloric acid. The sulphide (FeS) is readily obtained by heating three parts of iron filings with two parts of sulphur; an amorphous mass is left, which, when acted on by acids, yields sulphuretted hydrogen gas.

Ferric oxide (Fe_2O_3) is a dark red powder, soluble in acids, forming ferric salts. This oxide forms several hydrates, which lose their water on heating. When iron rusts in moist air, a hydrate is formed, having the composition ($2Fe_2O_3,3H_2O$). The ferric salts can be prepared by dissolving the ferric oxide in acids, or by oxidising the ferrous salts with a few drops of nitric acid. If a piece of iron be placed in dilute nitric acid, rapid action takes place, and the iron dissolves. If strong nitric acid be used of specific gravity 1.45, no action takes place, the iron becoming what is called "passive." If, however, the surface of the iron be scratched or touched by a more electro-negative metal, rapid action at once commences. It is probable that the surface of the iron becomes coated with a film of magnetic oxide, which protects the under surface from further action of the acid.

Ferric chloride (Fe_2Cl_6) is a powerful deodorant and its solution is used as an antiseptic.

Zinc ($Zn=65.5$). Metallic zinc is never found native; it occurs in combination with sulphur as "zinc blende," and as carbonate of zinc in "calamine."

Zinc blende, or black jack as it is called by the miners, is found in considerable quantities in this country, but calamine is imported principally from Spain and the United States.

In order to obtain the metal, the ores are first roasted, which in the case of the blende causes the formation of sulphur dioxide and zinc oxide, and with the calamine causes the evolution of carbon dioxide, zinc oxide as before, being left behind.

$$\overset{\text{Zinc blende}}{2(ZnS)} + \overset{\text{Oxygen}}{3O_2} = \overset{\text{Sulphur dioxide}}{2(SO_2)} + \overset{\text{Zinc oxide.}}{2(ZnO).}$$

$$\overset{\text{Calamine}}{ZnCO_3} = \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Zinc oxide.}}{ZnO.}$$

This zinc oxide is then mixed with finely powdered coal, and is heated in fire clay retorts, when, at a red heat, the metallic zinc distils over, and is condensed.

$$\overset{\text{Zinc oxide}}{ZnO} + \overset{\text{Carbon}}{C} = \overset{\text{Carbon monoxide}}{CO} + \overset{\text{Zinc.}}{Zn.}$$

In all the processes for extracting zinc, the general chemical reactions are the same, but different forms of furnace, retorts and receivers are employed.

In the English process, now but little used, the mixture of zinc oxide and half its weight of small coke is placed in a large earthenware crucible holding about $\frac{1}{4}$ of a ton; the lid of the crucible is then luted on, whilst a wide iron pipe passes through a hole in the bottom of the crucible and leads down into a space below the furnace. Each furnace holds about six of these crucibles, and on firing, as the temperature rises, decomposition takes place and the carbon monoxide escapes through the open pipe and burns with its characteristic blue flame on coming in contact with air. This flame is watched, and at a bright red heat the flame begins to show a greenish white tint due to the vapour of zinc, which is now distilling over. A second length of tube is now attached to the end of the first, and the zinc vapour condenses in the atmosphere of carbon monoxide and runs down and collects in a vessel placed to receive it.

The process most in use is known as the "Belgian process," in which the oxide, generally prepared from calamine, is distilled with carbon in fireclay cylinders, holding 40 to 50 lb. each, from the mouth of which the zinc vapour is conveyed by a short conical iron pipe into a conical iron receiver, which is removed and emptied every few hours. Forty or fifty of such retorts are built up in tiers in each furnace, and each distillation takes about twelve hours (Fig. 56).

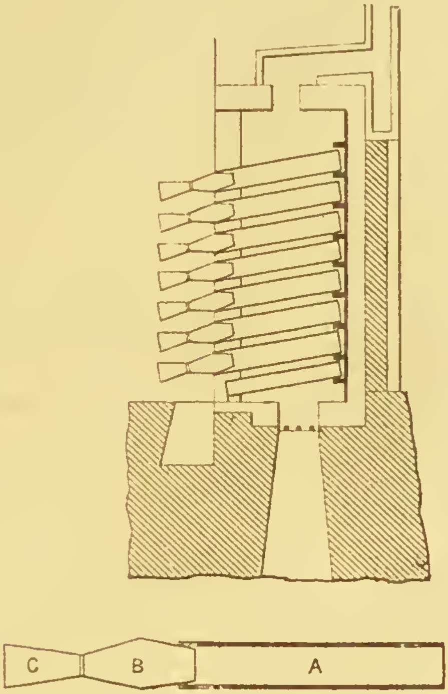

Fig. 56.

In the Silesian process the retorts employed are elliptical instead of round, the retort and condensing pipe being made in one piece.

Zinc is a bluish white, hard, lustrous metal. At ordinary temperatures zinc is brittle, but when heated to about 150° C.

it is both malleable and ductile. It melts at 412° C., and volatilises at 1040° C. Its specific gravity is about 7.0, varying from 6.8 to 7.1. Zinc undergoes very little change in air, but in contact with water charged with carbon dioxide it becomes coated with a film of oxycarbonate of zinc. When strongly heated in air or oxygen it burns with a bluish white flame, forming zinc oxide. One of the chief applications of zinc is for coating iron, in order to protect the latter metal from the corrosive action of moist air. Iron so coated is called "Galvanised Iron," and when exposed to air the outer surface of the zinc becomes converted into zinc oxide, which slowly forms a basic carbonate by absorbing carbon dioxide, and this thin film not being porous protects the metal below it from further action.

The iron to be coated is first cleansed from all oxide by pickling it in diluted acid, either sulphuric or hydrochloric being used for this purpose; it is then well washed, dried over a coke or charcoal fire, coated with ammonic chloride, and plunged into a bath of molten zinc, the surface of which is protected from oxidation by being coated with ammonic chloride.

Under these conditions the zinc forms a firmly adhering coating to the surface of the iron and protects it until an abrasion of some portion of the zinc surface takes place, when in the presence of moisture and carbon dioxide galvanic action is set up between the zinc and iron, and the zinc being electro-positive is rapidly dissolved away.

Zinc is readily attacked by acids, forming salts which are soluble in water. The sulphate ($ZnSO_4$) is isomorphous with magnesium sulphate, and this has led to fatal mistakes, the former salt being poisonous. In small quantities it is used in medicine as an emetic. Zinc chloride is a white deliquescent solid, and is used as a caustic. It is also used as a disinfecting agent (Sir W. Burnett's fluid), to absorb the offensive gases emitted by organic matter during putrefactive decay, such as ammonia gas, and sulphuretted hydrogen. The chloride is also used to clean metallic surfaces which are to be soldered together.

Cadmium (Cd=112) is always found in small quantities associated with *zinc* in its ores, and strongly resembles *zinc* in its physical and chemical properties; it melts at 228° C., and is converted into a vapour at 860° C.

The metal itself is sometimes used in fusible alloys, but its chief use is in the form of the sulphide which is used as the pigment "cadmium yellow."

CHAPTER XXIII.

METALS (*continued*).

Antimony and its compounds—Bismuth—Fusible alloy—Tin—Extraction of tin from tinstone—Properties of tin—Tinplate—Copper—Metallurgy of copper—Properties of copper—Lead—Action of water on lead—Bullets and shot—Oxides of lead—White lead—Alloys and their properties.

ANTIMONY (Stibium, Sb=122) is a very brittle crystalline metal, having a density of 6.7. It is rarely found native, but occurs principally as trisulphide in the ore called Stibnite (Sb_2S_3.) The metal is obtained on a large scale by heating the trisulphide with half its weight of metallic iron, when ferrous sulphide and metallic antimony are obtained :—

$$\underset{\text{Antimony sulphide}}{Sb_2S_3} + \underset{\text{Iron}}{3Fe} = \underset{\text{Ferrous sulphide}}{3(FeS)} + \underset{\text{Antimony.}}{Sb_2}.$$

Antimony undergoes no alteration in the air at ordinary temperatures, but if heated up to 450° it melts and rapidly oxidises; if heated more strongly, it takes fire and burns with a white flame, giving off dense white fumes of antimony trioxide. Antimony is not attacked by dilute hydrochloric or sulphuric acids. Nitric acid attacks the metal, dense red fumes of the lower oxides of nitrogen are given off, and a white insoluble powder is left behind, called antimony pentoxide.

The alloys of antimony are largely used in the arts. Of these type metal (antimony and lead), Britannia metal and pewter, are the most important.

Antimony combines with oxygen, and the halogens in two proportions forming antimonious and antimonic compounds.

Antimony trioxide (Sb_2O_3) is obtained by burning the metal in air, or by decomposing antimony trichloride with an alkaline carbonate.

$$\overset{\text{Antimony trichloride}}{2(SbCl_3)} + \overset{\text{Sodic carbonate}}{3(Na_2CO_3)} = \overset{\text{Antimony trioxide}}{Sb_2O_3} + \overset{\text{Sodic chloride}}{6(NaCl)}$$
$$+ \overset{\text{Carbon dioxide.}}{3(CO_2)}.$$

The trioxide dissolves, when boiled with a solution of cream of tartar, forming the substance known in medicine as "tartar emetic."

Antimony pentoxide (Sb_2O_5), is obtained by acting on the metal with nitric acid. It is a light straw coloured insoluble powder, decomposed on heating above 300°, yielding a lower oxide.

Antimony trichloride ($SbCl_3$)—sometimes called butter of antimony—is formed when powdered antimony is thrown into chlorine gas, or by dissolving the trisulphide in hydrochloric acid.

$$\overset{\text{Antimony trisulphide}}{Sb_2S_3} + \overset{\text{Hydrochloric acid}}{6(HCl)} = \overset{\text{Antimony trichloride}}{2(SbCl_3)} + \overset{\text{Sulphuretted hydrogen.}}{3(H_2S)}.$$

This method is used for the preparation of sulphuretted hydrogen, when the gas is required free from hydrogen.

If a solution of antimony chloride be mixed with much water, a white precipitate of the basic chloride is obtained.

$$\overset{\text{Antimony trichloride}}{SbCl_3} + \overset{\text{Water}}{H_2O} = \overset{\text{Antimony oxychloride}}{SbOCl} + \overset{\text{Hydrochloric acid.}}{2(HCl)}.$$

This property is a very curious one, and is common to several of the metals.

The trichloride is used extensively to produce the brown surface on steel in guns, which prevents rust. Antimony pentachloride is prepared by saturating the trichloride with chlorine; it is decomposed easily by water, or by heating. It is used as a chlorinator, giving up its chlorine readily. The sulphides of antimony (Sb_2S_3 and Sb_2S_5) can be precipitated from solutions of corresponding salts by hydric sulphide. The trisulphide so precipitated is of an orange red colour, and is employed for vulcanising caoutchouc. If this red sulphide be strongly heated, it becomes permanently grey, and resembles the natural black sulphide of antimony.

Bismuth ($Bi=210$) usually occurs native and in combination with sulphur, as bismuthite (Bi_2S_5). To obtain the metal the sulphide is roasted in the air, and the resulting oxide reduced with charcoal. Bismuth is a reddish white metal of specific gravity 9.9. It is permanent in air at ordinary temperatures, but rapidly oxidises at a red heat. It is brittle, and may be easily pulverised. It melts at 268°, and, like water, expands at the moment of solidification. The solidified metal has a pronounced crystalline structure, taking the form of rhombohedra in shape, closely approximating to cubes. It is very soluble in nitric acid, slowly soluble in sulphuric acid, and practically insoluble in hydrochloric acid.

The metal *per se* is not used in the arts, but is employed as an admixture in various alloys, most of which are remarkable for their low melting points. Rose's metal is an alloy which melts at 94°, and consists of 2 parts bismuth, 1 part tin, and 1 part lead. This and other similar alloys, which, by varying the proportions of the constituents, can be obtained of very varying melting points, constitute the so called fusible metal, of which use is made to prevent explosions in boilers, a plate or plug of the alloy being let into the boiler, so that as soon as the temperature of the steam reaches the melting point of the alloy the plug fuses, and allows the steam to escape.

Bismuth dissolves in nitric acid, forming bismuth nitrate, nitrogen peroxide being evolved.

This .salt is soluble in water, but excess of water precipitates the basic nitrate.

$$\overset{\text{Bismuth nitrate}}{3Bi(NO_3)_3 5H_2O} + \overset{\text{Water}}{H_2O} = \overset{\text{Bismuth oxynitrate}}{Bi(NO_3)_3 Bi_2O_3 3(H_2O)}$$
$$+ \overset{\text{Nitric acid.}}{6(HNO_3)}.$$

This substance when dried, constitutes the so-called "flake white," or subnitrate of bismuth.

Bismuth chloride ($BiCl_3$) is formed when bismuth is dissolved in aqua regia, and like the nitrate and other salts, it is decomposed by much water, forming an oxychloride.

$$\overset{\text{Bismuth chloride}}{BiCl_3} + \overset{\text{Water}}{H_2O} = \overset{\text{Bismuth oxychloride}}{BiOCl} + \overset{\text{Hydrochloric acid.}}{2(HCl)}.$$

This substance is used as a cosmetic, and called "pearl white."

Tin (Sn=118) has been known and used from the earliest times. Pliny relates that the Phœnicians were in the habit of trading both with Spain and Great Britain for tin. In this country it still occurs abundantly in Cornwall, and is also found in considerable quantities in Malacca, India and Mexico. Its chief and only important ore is tinstone (SnO_2), which is dioxide of tin. The tinstone as found in England is nearly always mixed with a large quantity of foreign substances such as quartz, earthy matters, pyrites, &c., and in order to remove these it has first to undergo a series of preliminary operations.

The purer portions are picked out by hand and are put on one side, whilst the residue is crushed in stamping mills, and the lighter portions consisting of the earthy impurities are washed away by exposure to a stream of water. This also gets rid of some of the pyrites, as the tinstone being very hard remains in larger pieces than the more friable sulphides; and as the specific gravity of the tinstone is 6.5, which is far higher than that of any of the substances mixed with it; it is possible to successfully treat even the poorest ores by this process.

The washed ore is now roasted to expel arsenic and also to break up any of the mixed sulphides of iron and copper (pyrites) which may remain in it. These latter are left as oxide of iron and sulphide and sulphate of copper, and on allowing the roasted ore to stand exposed to the action of air and moisture, the sulphide of copper is converted into soluble sulphate which can be removed by washing with water.

The ore so treated now contains from 60 to 70 per cent. of tin and the metal is obtained from it by mixing it with one sixth of its weight of charcoal and a small quantity of lime; the mixture is then carefully heated in a reverberatory furnace. The carbon unites with the oxygen of the ore and escapes, while the metal separates:

$$\begin{array}{ccccccc} \text{Tinstone} & & \text{Carbon} & & \text{Carbon monoxide} & & \text{Tin.} \\ SnO_2 & + & C_2 & = & 2(CO) & + & Sn. \end{array}$$

The temperature is then raised, and the lime present forms a slag with any siliceous matter that may have been present in the ore, and this collects on the top, the metallic tin sinking through it, and being drawn off from the bottom. This metal is cast into ingots, and is purified by being heated just to the point of fusion; the pure tin melts first, and is collected apart from the less fusible and more impure "block tin."

It is a somewhat soft, malleable, and very white, lustrous metal. On exposure to a damp air it tarnishes very slowly, but at a red heat it burns to stannic oxide. On account of its resisting the action of water and air, it used to be employed for making plates, etc., for domestic use, before Wedgwood ware and china came into general use, and its most important application is now for coating iron plates, by which they are protected from rusting, and can be used for innumerable purposes for which the iron plate could not be employed.

Tin plate is an alloy of tin and iron, formed upon the surface of the latter metal. In the manufacture of tin plate, the greatest care is taken to have the iron plate of the purest metal, or steel plates as nearly homogeneous as possible, and they are then pickled in dilute sulphuric acid, so as to remove every trace of grease from their surface and are tempered, again pickled, washed and dried, and after careful scouring with bran, are freed from any trace of moisture by keeping them some time in a bath of melted tallow; and on withdrawing them from this, they are then dipped in a bath of melted tin, the surface of which is protected from oxidation by a layer of melted fat; after taking out and draining, they are then dipped a second time in the tin pot, and are finally placed in a bath of highly heated tallow, which causes the excess of tin to run down and collect on the lower edge of the plate, from which it is detached by a sharp blow.

About 8 lb. of tin are required to cover 225 plates, weighing 112 lb.

The crystalline appearance known as "moirée métallique," sometimes given to tin plate, is obtained by washing it with a mixture of dilute hydrochloric and nitric acids.

In coating the interior of copper vessels, which are to be used for food, with tin, the surface of the copper is rendered perfectly clean by rubbing it whilst hot with sal ammoniac (ammonic chloride), sprinkling it with rosin to prevent oxidation, and spreading the melted tin over the plate with a brush of tow. Small metal articles, like pins, which are made of brass wire, are coated with tin by boiling them with salt of tin, and a reducing agent, which causes the deposition of the metal in a thin layer.

Tin fuses at 228°C., has a specific gravity of 7.28, and when cast into a stick and bent, omits a harsh grating sound known as the "shriek of tin." It is very malleable at ordinary temperatures but has very little tenacity; at 200° C. it becomes brittle and breaks with a blow into "grain tin." Tin is one of the principal metals used in all white alloys. It forms two oxides—stannous oxide (SnO) and stannic oxide (SnO_2), and in the same way forms two classes of salts, in one of which it behaves as a dyad, whilst in the other it is tetrad.

The oxides of tin have a very feeble basic action, whilst stannous chloride ($SnCl_2$) is a powerful reducing agent.

Copper ($Cu=63.5$) has been known from earliest times, being used for making tools and weapons long before any methods were discovered for the extraction of iron from its ores. It derives its name from the island of Cyprus. It is found native in the metallic form in Wales, Cornwall, and more abundantly in Siberia and South America.

The most important ore of copper is "copper pyrites," which is a double sulphide of copper and iron, which, when pure, may be represented as ($CuFeS_2$); it is nearly always, however, mixed with arsenical pyrites and other minerals, the percentage of copper which it contains varying considerably. The rich Bratzberg ore from Norway containing as much as 23 per cent. of the metal, whilst the ordinary grey Cornish ore contains about 6 per cent.

Amongst the other less important ores of copper are malachite, a basic cupric carbonate ($CuCO_3CuH_2O_2$), red copper ore or cuprous oxide (Cu_2O), and black oxide (CuO) found in the north of Chili.

The grey Cornish ore is the one chiefly used for the extraction of the metal in this country, and the process employed for the extraction of the ore is somewhat complicated.

The copper pyrites, consisting of copper and iron sulphides, is first carefully calcined or roasted for twelve hours. During this process the iron becomes oxidised, a portion of the sulphur volatilises and goes off as sulphur dioxide gas, together with fumes of arsenic, which is present in the pyrites, and it is the presence of these that render the "copper smoke," as it is called, so deleterious. The next part of the process consists of freeing the cuprous sulphide, formed in the roasting, from ferric oxide; this is accomplished in the ore furnace. Siliceous matter is roasted with the ore, and forms a slag of silicate of iron, which is raked off, whilst the "coarse metal," consisting of cuprous sulphide and ferrous sulphide, remains.

The third process consists in again roasting as at first, so as to oxidise the remaining ferrous sulphide, and again the oxide of iron is removed as slag by fusing with siliceous matter.

In this fourth operation, copper sulphide is left, and this is partly oxidised by roasting in a current of air, so as to leave a mixture of copper oxide and sulphide, and the copper oxide then reacts on the sulphide. Sulphur dioxide again escapes and metallic copper is left behind.

$$\overset{\text{Copper oxide}}{2(CuO)} + \overset{\text{Copper sulphide}}{CuS} = \overset{\text{Copper}}{3Cu} + \overset{\text{Sulphur dioxide.}}{SO_2}.$$

The melted copper is run into sand moulds, and as it cools, considerable quantities of sulphur dioxide escape from it, giving it a blistered appearance. The copper, so formed, is very impure, containing only about 95 per cent. of metal, the remaining 5 per cent. consisting mainly of iron, tin, arsenic and sulphur, and these are got rid of by the process of refining. The copper is melted and heated for some time, which drives off the sulphur and arsenic as oxides, and a scum of oxide of copper forms on the surface of the metal. It is then covered with finely powdered carbon to keep out the air and prevent further oxidation, and the molten metal is stirred with a green pole of birch or oak; the gases escaping from which reduce the oxide to metallic copper.

Copper has a specific gravity of 8.92; it melts at about 1100° C., and expands as it solidifies; it is very malleable, and can be beaten out to thin leaf, or drawn out into wire. In tenacity or strength it ranks next to iron, but it is very inferior to it; a copper wire, $\frac{1}{10}$th inch in diameter, will only support between 380 and 390 lb., whilst a similar iron wire will carry just over 700 lb. It is a good conductor of heat and electricity.

When copper is in the molten state it can absorb various gases, such as carbon monoxide, which escape as the metal solidifies, rendering the mass porous; consequently pure copper is rarely used for castings.

Copper is very largely used in alloys with other metals; the most important being brass, which consists of copper and zinc in the proportion of two to one. This alloy is made by melting zinc, and adding copper in small portions at a time; or by passing the vapour of zinc over heated copper. The various alloys used to imitate gold—before the art of electro-gilding was introduced—were all modifications of brass, and included Dutch metal, bronze powder, Pinchbeck, Prince's metal and mosaic gold. When brass is intended for engraving, a little tin is added, which causes it to break up more easily under the tool. The addition of a little lead, on the other hand, facilitates the working of brass in the lathe. In the manufacture of philosophical instruments, the brass work is protected from tarnishing in air by lacquering it with a coat of shellac varnish. The brass is sometimes bronzed—as in the sights of guns—which is done by applying a mixture of platinum chloride, corrosive sublimate and vinegar.

Copper resists the action of pure water or dry air, but when exposed for a length of time to moist air, the surface first becomes dimmed by a thin coating of oxide of copper, and this then takes up carbon dioxide from the air and is converted into a basic carbonate of copper, often erroneously called "verdigris." This action has occasionally led to very serious results from the use of copper vessels for culinary purposes; clean bright copper surfaces are not affected by the preparation of food in contact with them, but the oxide or carbonate is readily dissolved by such substances, and is a virulent poison.

At a red heat copper readily oxidises in air, forming the black cupric oxide (CuO). This oxide rapidly dissolves in acids to form stable salts, which are of a blue colour. Of these the most common is the sulphate or blue vitriol ($CuSO_4 5H_2O$). This salt on being heated loses its water and becomes white.

Sulphate of copper is much used by the dyer and calico printer; besides which, it is employed as the source of copper in the electrotype process, and also in certain forms of galvanic battery.

If a cupric salt be boiled with a reducing agent such as grape sugar in the presence of an alkali, a red powder is obtained consisting of cuprous oxide (Cu_2O). This oxide is very unstable. It is dissolved by melted glass, and imparts to it a ruby colour. The cuprous compounds are generally colourless and insoluble in water; readily soluble in ammonia and hydrochloric acid, absorbing oxygen rapidly and yielding cupric compounds.

A clean piece of iron immersed in an acid solution of copper, soon becomes coated with a red deposit of metallic copper; a corresponding amount of iron being dissolved. All cupric compounds are poisonous, and many are used as pigments.

Lead (Plumbum, $Pb=207$) is bluish white or grey in colour; it is extremely malleable, and is ductile, but is of slight tenacity; it is so soft that it may be easily cut with a knife, and leaves a mark if rubbed on paper. Lead expands greatly when heated; and does not on cooling always return to its original dimensions. It melts at 334°, and partially volatilises at a bright red heat. The metal slowly oxidises in moist air, and, consequently, clean surfaces soon tarnish. Lead in contact with aërated water soon becomes oxidised forming the white hydrated monoxide $Pb(HO)_2$, which is slightly soluble in water; the corrosive action is increased if ammonium salts are present, but is retarded by the presence of sulphates, phosphates and carbonates, owing to the formation of insoluble salts which coat the surface of the metal with a thin film, and protect it from further action. A large excess of carbon dioxide will, however, even then, increase the solvent action. This action of some waters on lead prevents this metal being used either for storing or distributing the water, as the dissolved lead salts are very poisonous, and act as a cumulative poison in the system. Lead cisterns should never be used for storing rain water. Lead is employed in several alloys. Type metal is composed of seventy five parts of lead and twenty five of antimony.

The high specific gravity as well as the fusibility of lead recommend it for the making of projectiles for small arms. Rifle bullets are made of very pure soft lead, in order that they may easily take the grooves of the rifle. In rifled ordnance, where iron projectiles are used, the surface of the shell is thoroughly cleansed, dipped into a solution of sal ammoniac, then into melted zinc, and is then coated with metallic lead. The coating of zinc causing a firm adhesion between the iron and the lead. Bullets intended to be discharged from smooth bore small arms, are hardened by the addition of 20 per cent. of antimony, in order to give them greater penetration. In the manufacture of small shot for fowling pieces, the lead is alloyed with about 5 per cent. of arsenic, which enables the lead to take a spherical shape when the melted metal is dropped through a colander into water. It is necessary, however, to cool down the drops before they fall into the water, and this is accomplished by allowing the molten metal to drop from a height of 100 to 150 feet, according to the size of the shot, through the air. It is probable that the presence of arsenic diminishes the power of the liquid lead to contract as it cools after the outer surface has solidified. The shot are dried on a hot plate, and polished by friction in a revolving drum containing a small quantity of plumbago.

The metal rarely occurs native, its chief ore is galena or lead sulphide (PbS). The general method of obtaining the metal from this ore is called the air reduction process.

The galena is first roasted in the air, and a portion is oxidised to oxide and sulphate :—

$$\overset{\text{Lead sulphide}}{\mathrm{PbS}} + \overset{\text{Oxygen}}{3\mathrm{O}} = \overset{\text{Lead oxide}}{\mathrm{PbO}} + \overset{\text{Sulphur dioxide.}}{\mathrm{SO_2}},$$

and,

$$\overset{\text{Lead sulphide}}{\mathrm{PbS}} + \overset{\text{Oxygen}}{4\mathrm{O}} = \overset{\text{Lead sulphate.}}{\mathrm{PbSO_4}}.$$

The mass is then thoroughly stirred ; the doors of the furnace are shut so as to exclude the air and the temperature is again raised. The oxide and sulphate now react on the remaining sulphide forming sulphur dioxide and metallic lead :—

$$\overset{\text{Lead oxide}}{2(\mathrm{PbO})} + \overset{\text{Lead sulphide}}{\mathrm{PbS}} = \overset{\text{Lead}}{3\mathrm{Pb}} + \overset{\text{Sulphur dioxide.}}{\mathrm{SO_2}},$$

and

$$\overset{\text{Lead sulphate}}{\mathrm{PbSO_4}} + \overset{\text{Lead sulphide}}{\mathrm{PbS}} = \overset{\text{Lead}}{\mathrm{Pb_2}} + \overset{\text{Sulphur dioxide.}}{2(\mathrm{SO_2})}.$$

Oxygen combines with lead in five proportions, three of which are important Lead monoxide (PbO) is formed by the oxidation of metallic lead in air ; at a moderate heat a yellowish powder, called massicot, is obtained ; at a higher temperature, a reddish powder, which yields a crystalline mass called litharge, when fused. This oxide is the only one that forms salts; the salts of lead being easily obtained by acting on the oxide with the corresponding acid, *e.g.* :—

$$\overset{\text{Lead oxide}}{PbO} + \overset{\text{Acetic acid}}{2(HC_2H_3O_2)} = \overset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + \overset{\text{Water.}}{H_2O};$$

$$\overset{\text{Lead oxide}}{PbO} + \overset{\text{Nitric acid}}{2(HNO_3)} = \overset{\text{Lead nitrate}}{Pb(NO_3)_2} + \overset{\text{Water.}}{(H_2O)}.$$

The monoxide is largely used in the Arts in the manufacture of lead pigments, of lead plaster, of glass, &c.

Red lead or minium (Pb_3O_4) is a bright red heavy powder, prepared by prolonged heating of the monoxide at a dull red heat in a current of air. It appears to be a compound of two molecules of monoxide and one molecule of dioxide of lead; for if red lead be acted on by nitric acid, the acid dissolves out the monoxide to form lead nitrate, and the dioxide is left as a brown powder. Red lead is largely used as a pigment, and in the manufacture of glass. It is frequently adulterated with brickdust, oxide of iron, &c.

The dioxide, or lead peroxide (PbO_2), is best prepared from red lead, as stated above :—

$$\overset{\text{Red lead}}{Pb_3O_4} + \overset{\text{Nitric acid}}{4(HNO_3)} = \overset{\text{Lead nitrate}}{2(Pb(NO_3)_2)} + \overset{\text{Lead dioxide}}{PbO_2}$$
$$+ \overset{\text{Water.}}{2(H_2O)}.$$

The dioxide is left as a dark brown heavy powder. When heated strongly it gives off half its oxygen, and the monoxide is left.

If heated with hydrochloric acid, lead chloride and chlorine gas are formed :—

$$\overset{\text{Lead dioxide}}{PbO_2} + \overset{\text{Hydrochloric acid}}{4(HCl)} = \overset{\text{Lead chloride}}{PbCl_2} + \overset{\text{Chlorine}}{Cl_2}$$
$$+ \overset{\text{Water.}}{2(H_2O)}.$$

The most important salt of lead is the carbonate, known as white lead. This salt ($PbCO_3$), occurs native in the mineral cerussite. It is a very heavy powder, almost insoluble in water, but is more soluble if carbon dioxide be dissolved in the water. It is much used as a pigment, and possesses special advantages as such, on account of which, in spite of its very poisonous character, and that it is blackened by sulphuretted hydrogen, it has not been superseded by zinc white (ZnO) or baryta white ($BaSO_4$). White lead has the property of combining to a certain extent with oils and varnishes, and gives the paint the property of what is known as covering well. A great deal depends, however, on the way the white lead is prepared. (*See* Pigments).

Lead chloride ($PbCl_2$) is always formed when a chloride is added to a strong solution of a soluble lead salt :—

$$\underset{\text{Lead nitrate}}{Pb(NO_3)_2} + \underset{\text{Sodic chloride}}{2(NaCl)} = \underset{\text{Lead chloride}}{PbCl_2} + \underset{\text{Sodic nitrate.}}{2(NaNO_3)}.$$

The precipitated lead chloride is a heavy white crystalline substance, soluble in hot water. A number of oxychlorides are known, some of which are of value as pigments, *e.g.*, Pattinson's white oxychloride ($PbCl,OH$), and Turner's patent yellow ($PbCl_2,7PbO$) sometimes called "Paris," patent or mineral yellow.

Lead salts are easily distinguished by their turning black when brought into contact with sulphuretted hydrogen gas; in fact, a most minute trace of this gas is easily detected by holding a piece of moistened lead paper (made by wetting blotting paper with a solution of lead acetate) in the gas, the blackening being due to the formation of black sulphide of lead.

Of the 65 elements no less than 50 are metals, but very few of these are available for common use, owing either to their rarity or to the difficulty and expense of separating them from their ores. In industrial processes, therefore, it is sometimes difficult to find any single metal whose physical properties would adapt it for any particular work. Whilst it may be possible in certain cases to alter the physical state of the same metal, by tempering or varying the method of producing it, yet the individual character of the metal still remains, and the induced conditions are rarely permanent To meet the varied requirements, the properties of a metal are altered by fusing it with one or more other metals, forming what is known as an alloy. When metals are alloyed, chemical combination sometimes takes place, but generally a simple mixture is formed possessing physical and often chemical properties, different from those of the original bodies.

Matthiessen has shown that when metals are alloyed together, it is impossible to calculate and foretell the properties of fusibility, elasticity, tenacity, crystallisability, conductivity for heat, electricity and sound, etc., from those of the individual constituents, except in alloys composed of the metals, zinc, tin, lead or cadmium.

The following tables show the composition of the more important alloys :—

STANDARD ENGLISH COINAGE.

	Gold.	Silver.	Copper.	Tin.	Zinc.
Standard gold ...	91.66	—	8.33	—	—
,, silver ...	—	92.5	7.5	—	—
Bronze	—	—	95	4	1

COPPER ALLOYS AND BRONZES.

	Copper.	Zinc.	Tin.	Iron.
Brass	71.4	28.6	—	—
Dutch metal ...	84.6	15.4	—	—
Muntz's metal ...	60	40	—	—
Aich metal ...	60	38.2	—	1.8
Sterro metal ...	56	40	1.5	2.5
Gun metal ...	90	—	10	—
Bell metal ...	78	—	22	—
Speculum metal	66.6	—	33.3	—

WHITE METALS, SOLDER AND FUSIBLE ALLOY.

	Antimony	Bismuth	Copper	Tin	Lead	Nickel	*Zinc.*
Britannia metal	6.2	—	1.8	92	—	—	—
Rose's fusible alloy	—	50	—	25	25	—	—
German silver ...	—	—	40	—	—	30	30
Pewter, plate ...	7	2	2	89	—	—	—
Solder, fine ...	—	—	—	66.6	33.3	—	—
,, coarse ...	—	—	—	33.3	66.6	—	—
Type metal ...	25	—	—	—	75	—	—

Most metals may be fused together in every proportion; there are a few, however, that will only mix in definite proportions, *e.g.*, if zinc and tin be fused together and either be in excess of the right proportion, it will crystallise out separately from the alloy formed.

The fusing point of alloys is frequently very much lower than the melting point of any of the component metals. Fusible metal consists of a mixture of bismuth which fuses at 265°, lead at 325°, and tin at 220°, whilst the alloy formed melts at 98°. Potassium and sodium, both solids at ordinary temperatures, when alloyed together in their atomic proportions form a liquid.

Alloys containing mercury have received the distinguishing name of amalgams, and a description will be found under the head of Mercury.

CHAPTER XXIV.

METALS (*concluded*).

Mercury—Mercury salts—Silver—Properties of the metal—Pattinson's process for the extraction of silver from its ores—Silver salts—Action of light on certain silver salts — Photography: Wet process — Dry plate process—Development—Printing—Toning—Platinotype—Ferrotype and carbon processes—Gold—Platinum.

MERCURY (Hydrargyrum, Hg=200), also called quicksilver, occurs chiefly as sulphide in the mineral cinnabar (HgS), from which the metal is obtained by roasting; the sulphur burns off, and the mercury vapour is led along cool passages where it condenses. Mercury is the only metal which is liquid at ordinary temperatures. It is almost silver white, of bright metallic lustre, and extremely mobile. It freezes at $-40°$ and boils at $357.5°$, but volatilises at all temperatures. Metallic mercury is used for the manufacture of thermometers, barometers, and other physical apparatus; for the collection of certain gases, the preparation of mirrors, and for the extraction of gold and silver from their ores.

All the ordinary metals with the exception of iron and platinum dissolve in mercury, yielding alloys which are known as amalgams. These amalgams are liquid at the ordinary temperatures if the mercury is in excess, but are otherwise solid or semi solid. If a piece of gold be brought into contact with mercury, the surface is instantly whitened, and after a time the gold becomes very brittle. In the manufacture of mirrors, the under surface of the glass is covered with an amalgam of tin and mercury. This is effected by laying a clean glass plate on a sheet of tin foil having a thin layer of mercury spread upon it. The excess of mercury is drained off, and after the lapse of a few weeks, a solid metallic coating is left on the glass, containing about 20 per cent. of mercury. For electrical purposes an amalgam of two parts of zinc and five parts of mercury is employed, whilst in dentistry, an amalgam of mercury with cadmium is often used.

Mercury forms two classes of compounds, namely, mercurous and mercuric. The mercurous are the most unstable, and have a great tendency to break up and form the higher compound and metallic mercury.

Mercurous oxide (Hg_2O), is a black heavy powder, easily decomposed by heat or light, prepared by precipitating a mercurous salt with caustic alkali.

Mercuric oxide, or red oxide of mercury (HgO), is a red crystalline solid when prepared by heating mercury in air for some hours to a temperature near its boiling point. If this red oxide be heated to a higher temperature, it splits up again into oxygen gas and mercury. When the oxide is prepared by precipitating a mercuric salt with caustic soda, it comes down as a yellow amorphous powder, and being in a finer state of division, is chemically more active than the crystalline variety.

The most important salts of mercury are the chlorides. To prepare these, mercuric sulphate is taken; this is obtained by boiling mercury and sulphuric acid together:—

$$\begin{array}{ccccccccc} \text{Mercury} & & \text{Sulphuric acid} & & \text{Mercuric sulphate} & & \text{Sulphur dioxide} & & \text{Water.} \\ Hg & + & 2(H_2SO_4) & = & HgSO_4 & + & SO_2 & + & 2(H_2O). \end{array}$$

Mercuric sulphate is formed and sulphur dioxide gas is given off. The mercuric sulphate is crystallised out and ground up with sodic chloride, and the mixture heated up in a retort.

The mercuric chloride or corrosive sublimate, as it is sometimes called, distils over, and sodic sulphate is left behind. Mercuric chloride is a crystalline salt, soluble in water, very poisonous, and is used as an antiseptic. Mercurous chloride, or calomel (Hg_2Cl_2) is a white salt insoluble in water and dilute acids, readily decomposed by alkalis. It is prepared in the same manner as mercuric chloride, only to the mixture of mercuric sulphate and sodic chloride, some metallic mercury is added and an intimate mixture made. The mixture is distilled, calomel comes over, and is condensed in an atmosphere of steam, this causing the powder to fall in a fine state of division.

$$\overset{\substack{\text{Mercuric}\\ \text{sulphate}}}{HgSO_4} + \overset{\substack{\text{Sodic}\\ \text{chloride}}}{2(NaCl)} + \overset{\text{Mercury}}{Hg} = \overset{\substack{\text{Mercurous}\\ \text{chloride}}}{Hg_2Cl_2} + \overset{\substack{\text{Sodic}\\ \text{sulphate.}}}{Na_2SO_4}.$$

The iodides of this metal may be easily prepared by treating a soluble mercurous or mercuric salt with iodide of potassium, and are recognised by their characteristic colours, mercurous iodide being yellowish green, and mercuric iodide a brilliant scarlet, the latter salt is, however, soluble in excess of either potassic iodide or the mercuric salt.

The nitrates are readily prepared by dissolving mercury in nitric acid. If the mercury be in excess, mercurous nitrate is formed; if the acid be in excess, mercuric nitrate is formed. Both these salts are soluble in water.

If ammonia solution be added to a metallic salt, the oxide of that metal is generally precipitated, but with the salts of mercury this is not the case, for if a solution of mercuric chloride be added to ammonia, an amido compound is formed, in which one atom of the chlorine is replaced by the group amidogen (NH_2), and has the formula ($HgClNH_2$); the common name for this substance is "white precipitate." Mercuric sulphide may be precipitated by sulphuretted hydrogen from solution of a mercuric salt as a black precipitate and is insoluble in nitric acid. The native sulphide, cinnabar, is red, and when ground to a fine powder constitutes the pigment vermilion.

Silver (Argentum, Ag=108) occurs both native and as sulphide in silver glance (Ag_2S), as chloride in horn silver ($AgCl$). Large quantities are obtained from galena, the ore of lead, which contains traces of this metal. Sea water also contains minute traces of silver.

Silver is the whitest of all metals, and admits of the highest polish. It is the best conductor of heat and electricity. It is very ductile, and so extremely malleable that it can be beaten out into leaves that transmit a bluish light. Silver melts at about 1000°, and possesses the remarkable power of absorbing oxygen from the air while it is liquid, and giving off the gas again when it is solidifying. When a mass of molten silver is allowed to cool, the film of solid metal which is formed upon its surface is burst in several places by the escaping oxygen, forming beautiful cones. This phenomenon is called spitting, frequently causing a loss of the metal. Silver is rarely used in the pure state, as it is too soft, and is therefore generally alloyed with other metals, chiefly copper. English standard silver is an alloy containing 7.5 parts of copper to 92.5 of silver.

Silver is extensively used for coating other metals by electro deposition; the object to be plated being placed in a bath consisting of silver chloride dissolved in a solution of potassic cyanide; the object is connected with the negative pole of a battery, the positive pole being connected with a silver or platinum plate and immersed in the bath opposite the object to be plated. Silver is also much employed for silvering mirrors and reflectors. A flask or globe may be easily silvered by taking a solution of silver nitrate, adding two or three drops of ammonia, then caustic potash, and lastly a solution of grape sugar in alcohol. On warming the contents of the flask gradually, the silver is reduced by the grape sugar, and deposits as a brilliant mirror on the inside of the flask.

On treating galena, all the silver present in the ore will be contained in the lead produced from it, and, if present only to the amount of a few ounces to the ton of lead, it may be profitably extracted by Pattinson's process. This consists in allowing the melted lead to cool slowly; now pure lead crystallises at a higher temperature than an alloy of lead and silver; crystals soon make their appearance in the mass, and these are removed by iron strainers as fast as they appear, until the greater part of the contents of the pot are removed in the form of crystals. These crystals are melted in a second pot, and separated by a second crystallisation, and the process is repeated several times, until the greater part of the silver collected in those portions of lead left after the removal ~~is~~ of the crystals of lead. The final purification is by the method of cupellation. The metals being exposed to a rapid current of air, after being heated on a layer of bone ash on the hearth of a reverberatory furnace. The lead rapidly oxidises, and is absorbed by the bone ash, the silver only remaining.

Silver does not combine readily with oxygen, and on this account is useful for coating other metals and for coinage, the tarnishing of silver being due to the presence of sulphur compounds in the air, which coat the silver with a film of the sulphide. Two oxides of silver are known; both are, however, very unstable, and also powerful oxidising agents. The monoxide (Ag_2O) is prepared by precipitating a solution of nitrate of silver with caustic alkalis: a brown earthy powder is obtained, excessively soluble in ammonia, and this solution evaporated at a gentle heat, yields crystals, probably of the composition ($AgNH_2$) which are most violently explosive at the slightest touch.

If silver monoxide be acted on by hydrogen peroxide, oxygen is given off, and metallic silver left.

$$\overset{\substack{\text{Silver}\\ \text{monoxide}}}{Ag_2O} + \overset{\substack{\text{Hydrogen}\\ \text{peroxide}}}{H_2O_2} = \overset{\text{Silver}}{Ag_2} + \overset{\text{Water}}{H_2O} + \overset{\text{Oxygen.}}{O_2}.$$

This reaction is of importance as showing the affinity of atom for atom to form the molecule.

Silver dioxide (Ag_2O_2) is a brown powder produced by the action of ozone on silver.

Silver nitrate ($AgNO_3$) is one of the most important salts of the metal. It is formed by dissolving silver in nitric acid, the salt crystallising in plates that contain no water. It melts at 193° without decomposing, and solidifies to a crystalline mass on cooling, and is called lunar caustic. The salt is used as a cautery, also for marking inks and in hair dyes. Silver combines with chlorine, bromine and iodine, and forms salts insoluble in water, but completely soluble in hyposulphite of sodium. These salts are easily prepared from nitrate of silver by precipitation with the chloride, bromide, or iodide of potassium.

These three compounds show, in a marked degree, the action of light on silver salts, namely, their instability under the action of white light. Certain parts of the spectrum, the blue end especially, have the power to decompose them, with the formation of subsalts, and for this reason have been employed most successfully in the processes of photography.

On studying the various parts of the solar spectrum, we find that different parts of it exhibit different properties, *e.g.*, the most refrangible or blue rays possess physical properties which readily start and support chemical action; whereas the rays at the red end do not possess this property; or, if so, only in a very slight degree. The red end of the spectrum, on the other hand, has greater illuminating power than the blue end. The rays at the blue end are termed the actinic rays. If such be allowed to fall upon a mixture of the two gases, hydrogen and chlorine, they combine and explosion takes place; whilst with certain compounds, such as the iodide, bromide and chloride of silver, decomposition takes place, small quantities of lower compounds being formed, and giving a dark colour to the salt which was originally white, or very pale yellow. It was upon this fact that, in a paper read before the Royal Society in January, 1839, Fox Talbot based his process of "photogenic drawing," which consisted of coating writing paper with a solution of salt, and this after drying, was brushed over with a solution of silver nitrate, forming silver chloride; on the surface so prepared he placed lace, ferns, &c., and by exposing to light, the uncovered portions were blackened, whilst those parts protected from light by the substance remained white. That is, he produced an outline of the object in white on a black ground, and he found that if now he dissolved away the undecomposed silver salts, and having dried his impression, used it to place over a second piece of prepared paper, he was able, on exposing once more to light, to obtain the outline in black on a white ground.

These two prints he respectively named the positive and negative, names which we use to the present time.

The silver salts most commonly used in photography are the chloride, iodide and bromide, and these are all combinations in which one atom of the silver metal is combined with one atom of the non metals, chlorine, bromine or iodine; when light acts upon these, some of the chlorine, bromine or iodine, as the case may be, is liberated, and a silver compound is left containing only one half as much of them as the salt originally taken, and these "sub-salts" being all dark coloured form the original image.

Silver chloride undergoes this alteration with considerable rapidity, silver bromide much more slowly, and silver iodide not at all unless some substance be present which will take up the iodine as it is liberated ; and this may be effected by adding to the silver iodide a little silver nitrate and gallic acid, which also renders the decomposition of the chloride and bromide much more rapid.

$$\underset{\text{Silver chloride}}{2(AgCl)} = \underset{\text{Silver sub-chloride}}{Ag_2Cl} + \underset{\text{Chlorine,}}{Cl,}$$

$$\underset{\text{Silver bromide}}{2(AgBr)} = \underset{\text{Silver sub-bromide}}{Ag_2Br} + \underset{\text{Bromine.}}{Br.}$$

A dark coloured compound will be formed by any of these mixtures after long exposure to light, but when only exposed for a short time, the amount of the original compound decomposed is so small that it is not visible to the eye, and in order to make it visible, it has to undergo a process known as "developing." The latent image may be rendered visible by taking advantage of the fact that the small quantity of sub-salt of silver formed during the brief exposure, although present in such minute quantity as to be invisible, yet can exercise sufficient chemical attraction upon metallic silver in the nascent state, as to cause it to be deposited from a decomposing solution of a silver salt upon those portions of the plate where the sub-salt has been formed.

Where the light has fallen most strongly upon the original sensitised material, there then will be the largest amount of the sub-salt, and when immersed in the developing solution this will have the greatest attraction for the depositing metal, and at these spots the darkest image will be found.

In the developing solution is present some substance with a strong attraction for oxygen, which will tend to cause the separation of finely divided silver. The solution of silver is already present in the wet processes, and in the old dry processes is added to the oxygen absorbing substance, which, as a rule is pyrogallic, acid or ferrous sulphate together with some acetic acid and alcohol, the acetic acid controlling the reduction of the silver nitrate.

In the early stages of photography, metallic plates were used to form the background for the thin film of silver salt, and then gradually paper began to be used, but the surface was too rough and uneven to receive sharp images, and the desirability of having a transparent background at once suggested glass; the trouble being, however, to form a thin coherent film of the silver salt on its surface; this was got over in 1851, by the discovery of the collodion process, which consists of dissolving an inferior kind of guncotton called collodion cotton ($C_6H_8O_3(NO_3)_2$) in a mixture of ether and alcohol, and allowing the solution to flow evenly over the face of a sheet of glass, the solvents evaporate and a transparent film is left on the surface of the glass. The collodion has dissolved in it a little iodide and bromide of potassium, and it is now rendered sensitive by immersing it in a solution of silver nitrate, when iodide and bromide of silver form in the pores of the collodion—the plate is then exposed, and the latent image developed by the reducing action of pyrogallic acid or ferrous sulphate solution.

The developed image being a metallic image will be permanent, but in order to prevent its being rendered indistinct by the undecomposed silver salts undergoing further decomposition, their removal is now necessary; and to do this advantage is taken of the solubility of the undecomposed silver salts in sodic hyposulphite or thiosulphate, so that by soaking the plate in a solution of this salt, called the "fixing bath," the image is rendered permanent.

This constitutes the old wet process, in which the plate has to be prepared, sensitised, exposed and developed within a very short period, unless it be specially prepared and protected. Within the last few years, however, a great advance has been made by the introduction of the so called dry plate process, in which the collodion is replaced by gelatine.

Such plates can be kept for months without deteriorating, and the development can be delayed after exposure to any convenient time. The plates also are much more rapid than those prepared by the collodion process (the ordinary gelatine plates being from 10 to 30 times, whilst special plates are made from 70 to 196 times as rapid). The preparation of dry plates requires some care, and of course all the operations must be conducted in a non-actinic light.

If bromide of potassium be dissolved in water, and a solution of nitrate of silver is now added, the precipitate rapidly settles to the bottom, and on stirring it up, it again settles when left at rest; if, however, a small quantity of gelatine is added to the water in which the bromide of potassium is dissolved, the precipitate of bromide of silver formed on adding silver nitrate does not settle, the colloid gelatine keeping it in suspension. If more gelatine were now added, an emulsion could be formed with which plates could be coated, but the action of light upon them would be excessively slow, and, in order to make them more sensitive, the original liquid with its small trace of gelatine is warmed for some time with a little ammonia at 35° C., or boiled with a small quantity of hydrochloric acid; this causes the particles of bromide of silver to aggregate into larger masses of definite form, a change which can be seen by transmitted light. The bromide of silver when first precipitated is orange by transmitted light, but as the warming proceeds, it gradually becomes lighter and acquires a blue tint which finally becomes grey; it should be stopped when the blue tint is reached, as at that point it is most sensitive, and if the required amount of gelatine be now added, a highly sensitive emulsion is produced, which sets on cooling. The bromide of potassium, when acted upon by the nitrate of silver, gave, by double decomposition, bromide of silver and nitrate of potassium, and the next step is to remove this latter salt which is in solution, and which, when a plate was coated with the emulsion would crystallise out and spoil the surface. This is done by breaking up the gelatine by pressing it through fine canvas or a syringe with holes in the bottom, and then dissolving out the nitrate of potassium by repeated washings with pure water, which dissolves the nitrate and leaves the gelatine and bromide of silver undissolved.

The gelatine with its bromide of silver is now melted, and a small quantity, not exceeding 10 per cent. of alcohol, is added to make it flow evenly over the surface of the glass, and a minute quantity of chrome alum, which has the effect of rendering the gelatine, after drying on the plate, much more insoluble in warm liquids, preventing its softening in warm weather, and also checking the so called "frilling" or puckering of the film of gelatine when immersed in liquids.

The plates after having been thoroughly cleaned, best by soaking in chromic acid, well washing with distilled water and drying, are now coated evenly with the emulsion and are placed in a perfectly horizontal position to set, care being taken that the air is dry and free from dust. When dry they are ready to be placed in the dark slide and transferred to the camera.

The plate having been exposed to light, and having received the image, is now ready for the second process, called developing.

There are three solutions at present in use for this purpose:—

1. Ferrous oxalate, made by adding one part of a saturated solution of ferrous sulphate, to three parts of a solution of neutral oxalate of potash.

2. Alkaline pyrogallate, in which pyrogallic acid is dissolved in the presence of some alkaline substance, such as ammonia, or sodic or potassic carbonate.

3. Alkaline hydroquinone.

All these three solutions are powerful reducing agents, and rapidly absorb oxygen. In order to check any too rapid action, and to prevent any of the unexposed salts of silver being reduced, a little potassic or ammonic bromide is added, and this acts as a restrainer and helps to prevent the plate from becoming "fogged," as it is termed.

The plate which has been exposed is now taken to the dark room and placed in one of the above developers; in a short time the image will begin to appear, and gradually gains in strength until all detail shows itself, provided the plate has been properly exposed, the exact time to stop development only being acquired by experience. The image now consists of silver reduced from the bromide. The developing solution is now washed from the plate by water and the unacted on compounds of silver are now removed by immersing the plate in a solution of sodic thiosulphate, until the lighter portions of the image are quite clear. The plate is now washed for some time in order to remove all soluble salts from the film and thus render it permanent. As before mentioned, all these operations must be conducted in a non-actinic light. If one of the gelatino bromide plates be exposed to the action of a spectrum, and then be developed, we find that the reduction only occurred in those portions that had been exposed to the green, blue and violet rays; the red, orange and yellow rays having little or no effect. Therefore, all preparation of emulsion, coating or developing a plate, must be done in darkness or by means of a light protected by yellow or red medium, such as ruby glass, or an orange coloured cloth called "golden fabric."

Having obtained the negative in which the lights of the original picture are reversed, it is easy to produce any number of positives by means of one of the many printing processes now in use. The simplest and most general method adopted is by employing a sensitised paper prepared as follows:—

The paper is floated on a mixture of albumen and chloride of ammonium, thus producing what is generally known as albuminised paper, and thus prepared will last for an indefinite period, and is not sensitive to light; in order to render it so, it is floated on a 10 per cent. solution of nitrate of silver, which forms in the albumen, chloride of silver and albuminate of silver; the paper after floatation is hung and dried, the sensitising and drying being carried on in yellow light. When dry, it is cut up to the required size and exposed under the negative; those portions of the negative which are opaque, allowing no light to pass through, the silver salts beneath remain undecomposed, the transparent portions of the negative allow the light to pass through, and there a darkening takes place; in this way, therefore, we have the image of the original produced in its proper gradation of light.

The next step is to remove all soluble salts by washing in ordinary water, and to tone the print.

If the undecomposed silver salts were removed by fixation, a disagreeable foxy red print would result; and in order to avoid this, recourse is had to what is called toning, which consists simply in gilding the reduced silver in the image, by immersing the print in a solution consisting of acetate of soda, chloride of gold, and water. The resulting colour will depend upon the time the print is kept in the solution, and also on the salt used in conjunction with the gold, the tungstate, phosphate and borate of soda, all giving different tints if used instead of the acetate. The print having been toned, is now rinsed in clean water and is transferred to a fixing solution, which is a 20 per cent. solution of sodic thiosulphate in water; in this the print is allowed to soak for 15 minutes so as to ensure the complete solution of the undecomposed silver salts —after this all soluble salts are eliminated by prolonged washing in running water, and the print after drying is ready for mounting.

Various other printing processes are also used, *e.g.*, platinotype and ferrotype photographs are made by taking advantage of the fact that ferric salts are converted by light into ferrous salts, and that these, when placed in a bath of chloroplatinite of potassium, reduce the salt, and platinum is deposited in a fine black powder on the portions of the exposed paper where the ferrous compounds have been formed.

In the ferrotype process, the paper with reduced iron salt is placed in a bath of potassic ferricyanide which gives a deep blue colour with the reduced iron salt.

In the so-called carbon process, advantage is taken of the fact that a mixture of gelatine and bichromate of potash becomes insoluble on exposure to light. If then a piece of paper be coated with a film of this mixture (the gelatine being coloured by suspending some pigment such as lamp black in it) and be exposed under a negative, where the light has penetrated, the gelatine will become insoluble, and on immersion in hot water, the unacted on portions will dissolve away and leave behind a positive picture composed of gelatine, rendered visible by the colouring matter suspended in it.

Gold (Aurum, $Au = 196.2$), is found widely diffused in Nature but in small quantity only. It occurs as nuggets, or disseminated in quartz veins in some of the oldest rocks. By the breaking and disintegration of these, gold sands are formed. In slight quantity it is found in the sand of almost every river. Many processes are in use for the extraction of the metal, and each depends on the particular way in which the gold is situated. From alluvial deposits or sand, it is obtained by washing away the light particles of sand and soil by means of water, the heavy gold particles remaining behind in the washing apparatus, or cradle as it is called; from the quartz rock, by reducing it to a fine powder in stamping mills, or by breaking the rock up by heating it strongly, and suddenly cooling by throwing it into cold water.

The powdered rock is then washed as described above, and the gold remaining behind, which has still some small pieces of rock with it, is extracted by means of mercury: an amalgam of gold and mercury is obtained, from which the gold is recovered by distilling the mercury off. Another process which has been lately proposed, is applicable for extracting gold when only occurring in very small quantities. The powdered quartz is heated with chlorine gas under hydraulic pressure (the chlorine for this process is made from bisulphate of soda and bleaching powder, two solid substances that can be carried about easily), the chlorine combines with the gold forming gold trichloride ($AuCl_3$), a very soluble yellow crystalline salt.

The metal is precipitated from this solution, completely, in form of a soft brown powder by ferrous sulphate:—

$$\overset{\substack{\text{Ferrous}\\ \text{sulphate}}}{6(FeSO_4)} + \overset{\substack{\text{Gold}\\ \text{chloride}}}{2(AuCl_3)} = \overset{\substack{\text{Ferric}\\ \text{chloride}}}{Fe_2Cl_6} + \overset{\substack{\text{Ferric}\\ \text{sulphate}}}{2Fe_23(SO_4)}$$

$$+ \overset{\text{Gold}}{Au_2}.$$

The precipitated gold is collected and refined by melting under a mixture of borax and nitre. Gold has little affinity for oxygen, and the oxides of gold can only be formed indirectly. This property of gold of resisting the action of oxygen in the air and not rusting, classes it as one of the noble metals.

Gold possesses a bright yellow colour by reflected light, and is the most malleable of all metals; if beaten out into thin sheets it transmits green light. It is not acted on by any single acid (except selenic), but dissolves in the presence of free chlorine, and in nitro-hydrochloric acid. Gold is nearly as soft as lead, so that it cannot be used for coinage in the pure state. The standard gold of our country being an alloy of 11 parts of gold to one of copper. For jewellery, pure gold is regarded as of 24 carats. An 18 carat gold, therefore, contains $\frac{18}{24}$ or $\frac{3}{4}$ths its weight of gold.

One of the most curious compounds of gold, is fulminating gold. This is prepared by acting on the trioxide (Au_2O_3) with aquous ammonia in excess, a yellow brown powder is obtained which, when dry, explodes very readily when heated to 100° or struck by a hammer. The composition of this substance is not accurately known, but is, no doubt, an ammonium compound, in which part of the hydrogen of the ammonium is replaced by gold.

By adding a mixed solution of stannous and stannic chloride to a solution of gold chloride a purple precipitate is obtained, which is called the "Purple of Cassius." The precipitate dissolves in melted glass, imparting to it a magnificent red tint, it is also used for painting on porcelain.

Platinum ($Pt = 194.5$) is only found native, that is in the metallic condition, but always alloyed with other metals. Its chief sources are the Ural Mountains, but it occurs also in very small quantities in Peru, California, &c.

The present method of working up platinum is to melt the ore in a very powerful furnace using the oxy-hydrogen blowpipe. In this way an alloy of platinum, iridium and rhodium is formed, the other constituents or impurities of the ore being absorbed by the lime of the crucible, or volatilised by the intense heat. This alloy is more useful than pure platinum, being harder and less easily attacked by acids than the pure metal.

Platinum is a white metal, does not tarnish in the air, is extremely infusible, and can only be melted by means of the oxy-hydrogen blowpipe. It also resists the action of any single acid, but dissolves in aqua regia, or chlorine water; for this reason platinum vessels, wire and foil are much used in the laboratory. Caustic alkalis, silicon, phosphorus and carbon, however, attack the metal at high temperatures; also several metals such as lead and antimony, form fusible alloys with the platinum. Vessels made of this metal should therefore never be brought in contact with these substances at an elevated temperature.

Molten platinum, like silver, has the power of absorbing oxygen and of giving it off again on solidifying. At a red heat the metal is readily permeated by hydrogen, but not by oxygen and the other gases. Another remarkable property this metal has, is the power to condense gases on its surface, this power, however, depends greatly on the physical condition of the metal. In a very finely divided state, as in the form of spongy platinum, or in the form of platinum black, many gases and vapours unite with oxygen in the presence of air, even at ordinary temperatures.

Platinum is tetravalent and combines with chlorine to form platinum tetrachloride ($PtCl_4$), a brownish red deliquescent salt, soluble in alcohol and ether, and is remarkable for the ease with which it forms double chlorides with the chlorides of the alkalis and alkaline earth metals and with the chlorides of many vegetable alkaloids. For this reason it is used to determine quantitatively the amount of potassium and ammonium present in different compounds. The double chloride of potassium and platinum has the formula ($PtCl_4,2KCl$).

CHAPTER XXV.

CORROSION, FOULING AND PIGMENTS.

The rusting of iron in air, fresh and sea water—Relative rate of corrosion of wrought iron and steel—Corrosion and pitting of marine boilers—Corrosion of ships' bottoms—Rust cones—Protective sheathing—Protective and anticorrosive compositions—Conditions under which protective compositions are placed—Corrosion in the interior of ships—Protectives for interiors—Fouling of ships—Copper sheathing—Action of sea water on copper—Antifouling compositions—Conditions of animal and vegetable life on a ship's bottom—Action of metallic poisons—Brackish water—Action of copper salts on a ship's hull—Properties necessary in a good antifouling composition—Pigments—Causes that affect colour—White lead—Zinc and permanent white—Blacks—Reds—Oxide of iron—Red lead — Vermilion — Carmine and lakes — Yellows — Red chromate—Gamboge, &c.—Green compounds of copper—Oxide of chromium—Compound greens — Blues — Ultramarine — Smalt—Prussian blue—Indigo—Raw and burnt umber—Sepia—Effect of light on watercolour paintings—Methods to ensure permanency.

WHEN iron is exposed to pure dry air no rusting of the surface takes place, but in moist air containing carbon dioxide corrosion rapidly commences, and continues at an increased rate until, if sufficient time be allowed for the action, the whole of the metal will be converted into mixtures of ferric oxide (Fe_2O_3) and hydrated ferric oxide ($Fe_2(HO)_6$).

Dry and pure oxygen alone has no action on iron and steel, moist pure oxygen acts only very slowly, and pure carbon dioxide when dry has by itself no action, but a mixture of the two in the presence of moisture rapidly sets up rusting of the metal.

When iron or steel is exposed to air, it is under these latter conditions, and contact being promoted by moisture, the carbon dioxide and oxygen simultaneously attack the metal, forming a thin and almost imperceptible layer of ferrous carbonate.

$$\overset{\text{Iron}}{Fe} + \overset{\text{Oxygen}}{O} + \overset{\text{Carbon dioxide}}{CO_2} = \overset{\text{Ferrous carbonate.}}{FeCO_3.}$$

The ferrous carbonate so formed is at once partially oxidised by more oxygen into basic carbonates and is finally converted into ferric oxide,

$$\overset{\text{Ferrous carbonate}}{2(FeCO_3)} + \overset{\text{Oxygen}}{O} = \overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Carbon dioxide.}}{2(CO_2),}$$

whilst if moisture be present in any quantity ferric hydrate is formed :—

$$\overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Water}}{3(H_2O)} = \overset{\text{Ferric hydrate.}}{Fe_2(HO)_6.}$$

During these reactions, the carbon dioxide is liberated in the moist metal and reacting with more oxygen from the air, carries on the process of corrosion, which is now further accelerated by the fact that the hydrated oxide on the surface of the metal is electro negative to the metal itself, and excited by the presence of moisture and carbon dioxide creates a galvanic current at the expense of the metal and the mass of rust formed being porous, the action continues until all the metal is destroyed and has returned to its natural condition of hydrated oxide.

In fresh water the corrosion which takes place on the surface of iron is due to the same cause, *i.e.*, the simultaneous action upon the metal of oxygen and carbon dioxide, and if an alkali be added to the water to absorb and neutralise all carbon dioxide, corrosion is stopped, and a piece of bright iron or steel may be kept perfectly uncorroded in such a solution.

If the dissolved oxygen is eliminated from the water, however, and the solution is saturated with carbon dioxide at ordinary pressure, and kept from contact with the air, the carbonic acid present will act directly upon iron or steel, forming ferrous carbonate and liberating hydrogen gas:—

$$\overset{\text{Iron}}{Fe} + \overset{\text{Carbonic acid}}{H_2CO_3} = \overset{\text{Ferrous carbonate}}{FeCO_3} + \overset{\text{Hydrogen.}}{H_2},$$

and this ferrous carbonate being soluble in the excess of carbonic acid present, the solution remains perfectly clear until air is admitted, when the ferrous salt at once is oxidised and the liquid turns brown, throws down a brown precipitate and forms a brown pellicle on its surface.

Sea water acts upon iron and steel in exactly the same way as fresh water, but the rapidity of the action is increased by the saline constituents of sea water, which undoubtedly play an important part in a more active form of corrosion, by helping to excite galvanic action between the iron in the plates and any foreign metal or impurities present, an action which is also materially aided by want of homogeneity in the metal, by particles of rust, by mill scale, by wrought and cast iron or steel in contact with each other; or even by the different amount of work, such as hammering or bending, undergone by different parts of the same plate; and in all of these cases, the galvanic action set up causes rapid oxidation of the iron at the expense of the oxygen of the water, hydrogen being evolved.

The main phenomenon of rusting in moist air/ fresh or salt water may, therefore be looked upon as the simultaneous action of water, carbon dioxide and oxygen upon iron. Besides this action, however, which takes place whenever iron or steel comes in contact with moist air, there are other local causes in many places which tend to increase corrosion.

Exposed iron work in a large city is subjected to the action of rain water containing sulphur acids washed from the smoke laden air, and these seriously increase the rate of corrosion. Again, a ship with her protective composition abraided in places by contact with chains, &c., cruises on the West Coast of Africa, where the rivers sweep down large quantities of vegetable and animal organic matter to the sea, which decompose the sulphates present in the sea water and charge the water with sulphuretted hydrogen, which attacks all metals with great rapidity.

These local causes of corrosion, however, have only to be taken into consideration where they occur and do not affect the general question.

One of the most important questions of the present day is, does steel corrode more quickly than iron and a very valuable research by Andrews* shows conclusively, that there is a greater tendency to corrosion on the part of all steels than wrought iron, when exposed to the action of sea water. The composition of some of the best known brands of plates was first carefully determined (*see Table*, page 429), and plates of known weight were then exposed to the action of sea water in presence of air, care being taken that no galvanic disturbances other than those set up on the surface of the plates themselves should interfere, and the plates were carefully cleaned, dried and again weighed after various periods of exposure; the loss in weight being taken as representing the loss by simple corrosion (*see Table*, page 430).

This table brings out very clearly the fact that there is a greater tendency to corrosion on the part of the various samples of steel than of the wrought iron, and also that the rate of corrosion increases very rapidly with the length of exposure, this latter being due to the fact that the oxides first formed are electro negative to the remaining metal, so that

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* Institution of Civil Engineers.

CHEMICAL ANALYSIS OF THE WROUGHT IRON, STEEL AND CAST METAL PLATES.

Description.	Graphitic carbon.	Combined carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Iron (by difference).	Total.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Wrought iron, No. 1 ...	—	Trace	0.206	0.024	0.454	0.396	98.92	100
,, ,, No. 2 ... (Wortley best scrap) ...	—	None	0.392	0.034	0.27	0.194	99.11	100
Soft Bessemer steel ...	—	0.15	0.015	0.111	0.064	0.54	99.12	100
Soft Siemens-Martin steel	—	0.17	0.071	0.117	0.077	0.627	98.938	100
Soft cast steel	—	0.46	0.074	0.025	0.21	0.184	99.047	100
Hard Bessemer steel ...	—	0.51	0.068	0.113	0.087	1.153	98.069	100
Hard Siemens-Martin steel	—	0.72	0.08	0.102	0.143	1.239	97.716	100
Hard cast steel	—	1.407	0.121	0.056	0.08	0.36	97.976	100
Cast metal, No. 1	1.5	2.01	0.41	0.25	0.45	0.65	94.73	100
,, ,, No. 2	2.62	0.67	1.94	0.09	0.95	0.52	93.21	100

Loss by Corrosion in Sea Water.

Description.	Combined carbon.	First period.	Second period.	Third period.	Total period.
		Loss per Square Foot of Surface.			
		Bright plates exposed singly in sea-water for 4 weeks.	Bright plates exposed singly in sea-water for 16 weeks.	Bright plates exposed singly in sea-water for 54 weeks.	Bright plates exposed singly in sea-water for 114 weeks.
	Per cent.	Grains.	Grains.	Grains.	Grains.
Wrought iron	—	—	—	—	—
Wrought iron, No. 1	Trace	34.4	114.68	169.7	318.78
Wrought iron, No. 2 (Wortley best scrap)	None	—	97.99	139.27	—
Soft Bessemer steel	0.15	34.56	108.85	158.18	301.59
Soft Siemens-Martin steel	0.17	40	125.83	155	320.83
Soft cast steel	0.46	35.76	148.65	227.74	412.15
Bessemer steel	—	—	—	—	—
Hard Bessemer steel	0.51	38.96	134.92	199.68	373 56
Hard Siemens-Martin steel	0.72	34.24	122.14	173.24	329.62
Hard cast steel	1.407	39.68	139.57	184.54	363.79
Puddled steel	—	—	—	—	—
Puddled steel (chilled)	—	—	—	—	—
Tungsten steel	—	—	—	—	—
Cast metal, No. 1	2.01	—	160.62	254.25	—
,, ,, No. 2	0.67	—	182.7	172.73	—
,, ,, No. 3	—	—	—	—	—

with the formation of rust galvanic disturbances are increased on the surface of the plate and tend to increase the rapidity of its destruction.

The probable reasons which tend to increase the rate of corrosion in steel are that it is not so homogeneous as the wrought iron, that the manganese is usually present in larger quantities and that the carbon present in combination is partly eliminated during corrosion in the form of carburetted hydrogen which tends to disintegrate the surface.

A very valuable paper read before the "Iron and Steel Institute" by Mr. Parker in 1881* also shows that mild steels such as are now used for boilers and for ship building suffer from corrosion more than the purer metal, but that the increase is not nearly so great as alarmists would have one believe.

To the Navy the most important cases of corrosion are those which affect the plates and tubes of marine boilers and the plates of the bottom of vessels, and inasmuch as the causes at work in these two cases are not identical it is better to discuss them separately.

In the marine boilers at present in use, working at pressures of from 50 to 250 lb., serious pitting and in some cases puncturing of the plates and tubes take place, a result which, before the introduction of hydrocarbon lubricators, was largely attributed to the corrosive action of the fatty acids liberated by superheated steam from the oils and fats used for the lubrication of the cylinders, but as the corrosion and pitting has continued since these lubricants have been discarded, and as the trouble increases with the increase in the pressures employed, it is evident that some other solution of the difficulty must be sought.

The pitting and corrosion are due not to one cause only, but to several acting together.

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* *Journal of the Iron and Steel Institute*, No. 1, 1881, p. 39.

1. Ordinary corrosion due to the carbon dioxide and oxygen dissolved in all natural water, which acts but little when the boiler is in use, the gases being driven off by the steam, but which acts rapidly when a boiler is out of use, more especially when, as used to be the case in the Navy, the water is partially blown off and the boiler left wet and exposed to air.

The simplest cure for this is, when a boiler is at rest, to fill it quite full with boiled water to which a little lime or other caustic alkali has been added.

2. One of the causes of pitting in a boiler is the formation of spots of rust from the previous cause which being electro negative to the metal rapidly cause it to corrode, and it is this action, and also the galvanic action of traces of metallic impurities which is to a certain extent prevented by zinc protectors, zinc being electro positive to both iron and oxide of iron, but for the protectors to be of any use they must be in metallic contact with the metal of the boiler.

3. The solvent action of distilled water upon metals, which, in modern marine boilers fed with condenser water and specially distilled water, rapidly attacks the plates in places where the presence of a trace of slag or other impurity renders the metal less dense or gives it a tendency to lamination. This can be avoided by using a saline solution such as the prepared sea water advocated at p. 125 for the prevention of incrustation and avoiding too frequent blowing off, the action of water on iron rapidly decreasing with an increase in its density.

4. The fact that at a high temperature, water is directly decomposed by iron with formation of black magnetic oxide and liberation of hydrogen :—

$$\begin{array}{ccccccc} \text{Water} & & \text{Iron} & & \text{Black magnetic oxide of iron} & & \text{Hydrogen.} \\ 4(H_2O) & + & 3Fe & = & Fe_3O_4 & + & 4H_2, \end{array}$$

an action, which, at a dull red heat is the cheapest method of obtaining the gas, and which takes place more slowly at temperatures considerably below dull red heat, and which are often approached, if not reached, on the surface of tubes coated with incrustation, where the moisture present rapidly acts on the metal and ultimately pierces it.

This latter cause of pitting can only be avoided by keeping the boiler free from all incrustation by using either distilled water or prepared sea water.

On the outer skin of an iron vessel two processes of rusting are going on, the one simple corrosion on exposed surfaces of the metal, due to the presence of moisture, carbon dioxide and free oxygen, which forms a fairly uniform coating of rust on the metal, and the more local corrosion due to galvanic action, which results in pitting and uneven eating away of the plates.

Rust cones are due to the most local form of galvanic action, caused by the presence of a speck of deposited copper, lead—or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and antifoulers; as soon as the sea water penetrates to these, galvanic action is set up; water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister, the hydrogen escapes and water leaks in, the action becoming more and more rapid, and the blister gradually filling with the result of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being easily distinguished in a well-formed cone, and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

The speck of foreign matter which has caused this destructive action generally clings to the surface of the iron, and being at the bottom of the pitting, escapes detection and removal; and when the vessel, newly coated with fresh compositions, again goes to sea, the corrosion will again probably be set up in the same spot.

The corrosion of the plates in the interior of a vessel is a subject quite equal in importance to the external action of sea water and dissolved gases on the metal; and from the fact that certain portions of the interior plates, from their position, escape the frequent examination and attention bestowed upon the exterior, it becomes a still greater source of danger.

Corrosion, like all other forms of chemical action, is much accelerated by increase of temperature; and in the bottom of a ship, near the furnace room and boilers, this has a considerable effect in increasing the rapidity of rusting. Also in the coal bunkers, the mere contact of moist coal with the iron plates sets up galvanic action, carbon being electro negative to iron, and the coal dust which sifts down into the double bottoms lends its aid to the destruction of the plates; whilst if the coal contains any "pyrites," which is nearly always the case, these double sulphides of iron and copper are gradually oxidised into soluble sulphates of the metals, and these, washing down into the bilge water, would at once cause most serious corrosion should they come in contact with any bare portion of the plates. Repairs to any portion of the inside plates will loosen rust and mill scale, which, finding its way into the bottom, tends to set up galvanic action; whilst the scale of oxide of copper from copper and brass fittings and pipes is another great cause of danger, as the bilge water would gradually convert it into soluble salts, which will deposit their copper upon the iron wherever a crack or abrasion enables them to come in contact with it; and finally, leakages from stores and cargo are in many cases of a character highly injurious to iron.

In addition to all these sources of danger, we must remember that the interior of the vessel is the part most liable to abrasion from shifting and moving of cargo, coals, &c.

The protection of the outsides of the bottoms of ships from the destructive agencies of sea water and dissolved gases may be said to have been attempted in two ways, by metallic and by non metallic coatings.

Zinc is practically the only metal which could be used for this purpose, in order to place the plates of the ship in an electro negative condition ; and it is, therefore, to zinc that inventors have turned from time to time, the chief novelties introduced being the method of attachment. As far back as the year 1835, Mr. Peacock tried zinc plates on the bottom of H.M.S. *Medea*, and in 1867 Mr. T. B. Daft again brought the subject forward ; Sir Nathaniel Barnaby, Mr. McIntyre, and others, also suggesting various plans of attachment, whilst lately Mr. C. F. Henwood read a paper at the United Service Institute again strongly advocating zinc sheathing as attached by his system.

There is no doubt that if a surface of iron is kept in galvanic contact with zinc, and the surface of zinc exposed be of sufficient size relatively to the iron surface to be protected, that it will act as a perfect protection against the more active forms of galvanic corrosion, but it will not entirely prevent the ordinary oxidation due to the dissolved gases in sea water ; and it must also be remembered that the salts in sea water have a fairly rapid action upon the zinc, which, when it is increased by the galvanic action set up by the enormous surface of iron present, would destroy the zinc sheathing too rapidly to render it a practical method, several cases having occurred in which an iron ship coated with zinc plates has returned from a voyage minus a considerable portion of her sheathing. If no galvanic contact exists the zinc sheathing will last fairly well, but does not afford any protection to the iron.

Attempts have been made to galvanise the iron before the building of the ship ; but Mr. Mallet showed as early as 1843 that this coating was absolutely useless in sea water, as in from two to three months the whole of the zinc was converted into chloride and oxide; but used as a foundation over which the ordinary protective and anti-fouling compositions are to be painted, galvanising acts as a perfect protective, the only trouble being that it affords but little hold for the compositions which have to be put on over it, so that a galvanised torpedo boat quaking along at 20 knots, requires a very adhesive composition to stick on. This objection could however be easily got over by a slight roughening of the galvanised surface so as to give the paints a "grip."

Certain alloys of zinc and copper which have but little galvanic action on iron, have been proposed as sheathing for iron but have never proved successful.

Copper itself has been of late used to a considerable extent as sheathing, being insulated from the iron by means of wood, but it has many disadvantages, which are discussed under "Anti-fouling."

Tin and lead have been proposed for coating ships, but, like copper, these metals are electro negative to iron, and would rapidly destroy the hull, should any abrasion of the coating take place.

The non metallic coatings, which are intended to do away with corrosion are very numerous. At the present moment there are upwards of 30 in the market; whilst the patent list of the last 50 years contains an enormous number which were practically still born.

They may be divided for convenience into—

(*a*) Oil paints.
(*b*) Pitch, asphalt, or tar.
(*c*) Varnishes, consisting of resins and gums dissolved in volatile solvents.
(*d*) Varnishes, containing substances to give them body.
(*e*) Coatings of cement.

And, before going into these in detail, it is necessary to consider the condition of the surfaces to which they will have to be applied, and the effect this will have upon them.

Air has the power of holding water vapour in suspension, the amount so held being regulated by the temperature; the higher the temperature the more vapour can the air hold, whilst when the air, saturated at a particular temperature, is cooled the surplus moisture is deposited. When a ship is scraped down to the bare iron in the dry dock, we have a large surface of metal which varies in temperature much more rapidly than the surrounding air, and cools much more rapidly than the stone walls of the dock; as it cools so it chills the layer of air in immediate contact with it, and causes a deposition of the surplus moisture on its surface—a phenomenon known as the "sweating of iron"—and on to this moist surface the protective composition has to be painted. If now a rapidly drying varnish is put on, the rapid evaporation of the volatile solvent causes another sudden fall of temperature—evaporation being always accompanied by loss of heat—and this fall of temperature again causes a deposition of moisture, this time on the surface of the protective, so that the coating is sandwiched between two layers of moisture, both of them probably acting deleteriously upon the resin or gum in the varnish, whilst the moisture on the iron also prevents adherence of the varnish to the metal. If, instead of a quick drying varnish, the old fashioned red lead and linseed oil protector had been used, the second deposition would not have taken place, but the sweating of the iron would have prevented cohesion, and, when dry, any rubbing of the coating would bring it off in strips.

The condition of the outer skin of a ship, when she is being coated with her protective composition, is one of the prime factors in the discrepancies found in the way in which compositions act. It being a very usual thing for a composition to give most satisfactory results on several occasions, and then, apparently under exactly similar circumstances, to utterly break down, and to refuse even to keep on. Too much stress cannot be laid upon the condition of the plates at the time of coating, and it is absolutely essential either to have a perfectly dry ship, or else a composition which is not affected by water.

When an old ship is broken up, the numbers are often seen on the backs of the plates, having been painted on them with white lead and linseed oil before the ship was built, and under the paint the iron is in a perfect state of preservation, the reason being that the paint was put on while the plates were hot and dry.

Boiled linseed oil, mixed with red or white lead, is amongst the oldest of the protective compositions in use, but of late years has been but little employed, since it was proved by M. Jouvin of the French Navy, and also in this country, that compounds of lead, when exposed by the wasting of the linseed oil to the action of sea water, are converted into chloride of lead, and this is rapidly acted on by the iron, depositing metallic lead and forming chloride of iron, the deposited lead carrying on the corrosion of the iron by rapid galvanic action. The drying of boiled linseed oil is due to the fact that it has in it a certain quantity of an organic compound of lead, and the drying properties are given to it by boiling it with litharge (oxide of lead), so that, even when red or white lead is not mixed with it, still lead compounds are present, and this action will go on to a smaller extent.

When the boiled oil drys, it does so by absorbing oxygen from the air and becomes converted into a sort of resin, the acid properties of which also have a bad effect upon iron, so that protectives containing boiled oil are open to objection. Lately, a good example of the action of sea water on the bottom of an iron ship, coated with red lead, has been afforded by H.M.S. *Nile*, which, after being painted over with coats of red lead, was allowed to remain for some months in Milford Haven, with the result that her bottom is very seriously corroded, and, on examination of specimens of rust taken from her, the crystals of metallic lead are in many cases easily identified.

If red lead is used, it can only form a ground work for an anti-fouling composition which has to protect the red lead as well as the iron of the ship from the action of sea water, and when the anti-fouling composition perishes then serious corrosion must ensue.

The second class of protectives, consisting of tar and tar products, such as pitch, black varnish, and asphalt, are amongst the best protectives, not being affected by the sweating of the plates, and forming admirable coatings. Certain precautions, however, must be taken in the case of tar and tar products, both of which are liable to contain small quantities of acid and of ammonia salts; but if care be taken to eliminate these, and if it could be managed to apply this class of protectives hot to warm plates, the question of protection would be practically solved, bituminous and asphaltic substances forming an enamel on the surface of the iron which is free from the objections to be raised against all other protectives, that is, that being microscopically porous they are pervious to sea water.

The third class of protectives, consists of varnishes formed by dissolving gums or resins in volatile solvents, such as spirit, turpentine, naphtha, fusel oil, &c., and such varnishes are open to several objections—in the first place, they are acted upon by moisture, which causes a deposition of the resins or gums as a non coherent powder, and destroys the tenacity of the varnish. The amount of action which moisture has on such a spirit varnish, depends to a considerable extent upon the proportion of resin or gum to spirit, when the solvent is present in large quantities, and the resin in comparatively small; then the moisture has apparently little action; but it must be remembered that the drying of such protectives means the rapid evaporation of the solvent and concentration of the resin or gum, whilst the rapid volatilisation which is going on cools the hull of the ship, and causes deposition of moisture on the drying varnish with most disastrous results.

Another point which must be borne in mind is that no such varnish is impervious to gases and liquids. We are apt to think of a coating of varnish as being perfectly homogeneous; but, on examining it through a microscope, it is seen to be full of minute capillary tubes, which become gradually enlarged by the action of water, and finally result in the destruction of the varnish, whilst moisture and dissolved gases find their way to the metal and carry on corrosion. The application of several coats of varnish tends to diminish this evil, as in many cases the holes in the first coat will not correspond with the holes in the second, and so each succeeding coat will tend to make the protective more and more impervious. In using such varnishes, they must only be applied in favourable weather, and must be allowed to thoroughly harden before being brought in contact with the water.

In the fourth class we have varnishes of this kind to which body has been given by the addition of foreign constituents, generally mineral oxides; and this class is far preferable to the last, if the solvent used is not too rapid in its evaporation, and if care has been taken to select substances which do not themselves act injuriously upon iron or upon the gums or resins which are to bind them together, and are also free from any impurities which could do so.

At present the favourite substance used to give colour and body to such varnishes is the red oxide of iron, the colour of which effectually cloaks any rusting which may be going on under it. In using the red oxide for this purpose, care should be taken that it contains no free sulphuric acid or soluble sulphates, as these are common impurities, and are extremely injurious, tending to greatly increase the rate of corrosion. The finest coloured oxides are, as a rule, the worst offenders in this respect, as they are made by heating green vitriol (sulphate of iron), and in most cases the whole of the sulphuric acid is not driven off as the heat necessary impairs the colour.

The best form of oxide of iron to use for this purpose is obtained by calcining a good specimen of hæmatite iron ore at a high temperature. When prepared in this way, it contains no sulphates, but from 8 to 40 per cent. of clay; if the percentage does not, however, exceed 12 to 18 per cent. it is unobjectionable.

A far better substance to use for this purpose would be the mixture of finely divided metallic zinc and zinc oxide, which can be obtained as an impalpable powder from the cones used to close the nozzles of the retorts used in the Belgian process of distilling zinc (p. 389). If a good sound shellac varnish had body given to it by this mixture, which usually contains about 80 per cent of zinc, no action would take place until the varnish had perished, and when this took place the zinc would set up galvanic action with the iron and afford the plates a further period of protection, leaving a spongy coating of zinc oxide behind on the metal which would again tend to protect it.

In the fifth class of protectives we have cement coatings; but these, together with such schemes as covering the hull of the vessels with vitreous glazes, glass, &c., have of late years been entirely abandoned. The action of cement on iron, however, must later on be discussed in its important bearing on the protection of the interior portions of the hull, for which it is largely employed, its weight and the difficulty of attachment rendering it unfitted for outside work.

In selecting a protective composition for the bottom of a vessel, one of the second or fourth class should be chosen, attention being given to the points indicated, which are that in the bituminous and asphaltic compositions all the original acids must be eliminated, and that in the varnishes of the fourth group quickly evaporating solvents should be avoided, and, if possible, zinc substituted for oxide of iron.

The vessel should have her plates as dry as possible during the application of the protective, and, if feasible, days on which the air is fairly dry, and a brisk breeze blowing, should be chosen. The protective should not be too thick, as, if it is, it does not readily fill into inequalities in the plates; and, if in this way any air is enclosed, change of temperature will cause it to expand or contract, thus causing a blister to form, which will fill with sea water and set up rapid corrosion. The composition must either be elastic or else have the same rate of expansion and contraction as the iron; for, if not, the change of temperature will cause cracking and tearing of the composition with disastrous results. The vessel, if she has to be scraped down to the bare metal, must be scrubbed free from all traces of rust, and where a well adhering coating of composition exists, it should be painted over and not disturbed. In the case of a new ship, she must be pickled with dilute acid, to get rid of every trace of mill scale, and then washed down with some slightly alkaline liquid to neutralise every trace of acidity, the alkali in turn being removed by clean water. Under these conditions, and given a composition with good adhering properties, but little apprehension need be felt as to the ravages of corrosion on the metal of a ship's bottom, the chief risk being from abrasion and other mechanical injury to the composition, coupled with improper constituents in the anti-fouling compositions.

The protection of the interior portion of the vessel, where the plates are exposed to the corrosive action of bilge water, rendered more active by a high temperature, leakage from cargo, acids and sulphates from wet coals, and the presence of such electro negative bodies as coal dust, scale and rust, is a matter of quite as great importance as the external protection; whilst the great risk of mechanical abrasion during coaling and shifting of cargo, as well as the difficulty of getting at the lower portions of the hold to examine the condition of the plates, renders adequate protection absolutely necessary. The corrosion found in the portions underneath the engine seats, the bunkers, and the water ballast chambers, especially near the engine room, is often very serious, and needs most careful watching, which, from the position of these parts of the vessel, it is very hard to bestow upon it.

It must also be remembered that the bilge water in a vessel is in constant motion, and that the air in these parts of the vessel may be expected to be exceptionally rich in carbon dioxide, which is the most important factor in corrosion. Under these conditions any abraded portion would probably be continually washed over, and then exposed to the foul air, a condition of things most conducive to rapid rusting. There are three main classes of protectives for the interior of a ship—

(1) Cements.
(2) Bituminous coatings.
(3) Paints.

The first of these, the cement coatings, have many good points to recommend them, but they also have many serious drawbacks.

The rigidity, firmness of adherence and endurance, are all of them points of the greatest importance, and there is no doubt but that the silicates present in the cement in time, not only bind the cement into a mass of great hardness, but also bind the cement to the iron. A thin coating of Portland cement, however, is highly porous, and can be permeated by liquids and gases. Suppose, now, that the oxidation of copper pyrites in the coal bunkers had given rise to some soluble sulphate of copper which had washed down into the bilge water; this solution would soak through the capillary orifices in the cement, until it came in contact with the iron below, when the copper would be deposited on the iron, and rapid galvanic action set up, the cement being loosened, and to a certain extent lifted, by the formation of rust, whilst corrosion would gradually extend under the cement, giving on the outside of the coating but little sign of the damage taking place below it.

That this is a real danger is proved by the fact that on several occasions a deposit of metallic copper has been found under the cement and in contact with the iron.

Also the hardness and rigidity of the cement give it a tendency to crack away from the metal when any strain is thrown on the plates, or during any expansion or contraction of the metal; whilst any repairs on the outside of the ship, such as making a boring to test the thickness of plate, replacement of rivets, &c., would undoubtedly cause a loosening of the cement coating within, and, wherever a loosening takes place, the space between the cement and the plate will quickly be found to become a starting point for corrosion, which quickly spreads and loosens the cement, and will only be discovered by chance.

It is for this reason that bituminous or asphaltic varnishes, freed from any trace of acid and applied hot, or sound tough paint, are preferable to cement; as, although they are not so hard, yet if serious corrosion should be set up, it is easily discovered and stopped before much damage results, whilst, being impervious to moisture, deleterious solutions, either from the coal bunkers or cargo, would be prevented from acting upon the skin of the ship.

In approaching the subject of fouling, one is impressed with the apparent hopelessness of obtaining any reliable information from the successes or failures registered by the bottoms of the vessels in the Service, or in the Mercantile Marine. Hundreds of ships may be examined, and their condition and the nature of the compositions used upon them registered, and just as one begins to feel that the key to the mystery is within one's grasp, a whole series of results so abnormal suddenly comes to light that it seems impossible to reconcile them with one's previous experience. A ship may sail half a dozen times to the same waters, coated with the same composition—on four occasions she will come home clean and in good condition, whilst on the other two voyages she may accumulate an amount of weed and animal life sufficient to reduce her speed from nine knots to five. Moreover, if the compositions with which she was coated be examined, and scrapings taken from her on her return, no cause will present itself that can in any way explain the great difference in her condition. After several years' close observation, however, certain factors begin to make themselves apparent. Certain seasons of the year give rise to more fouling than others, according to the waters in which the ship has been; one also begins to realise that the amount of fouling increases enormously if the ship has been long at anchor—ships which have been lying at the mouths of rivers, although quite clean in the brackish water, foul much more rapidly on going to sea than vessels which have been cruising, or even at anchor for the same time, in salt water; and, finally, certain ports and certain seas seem to exercise a deleterious effect, both as regards corrosion and fouling, which is not to be found elsewhere.

Turning back to the naval history of the past, we find that fouling is no new trouble born with the advent of our present iron monsters; but that it has been the one trouble that the combined engineering and scientific skill of many centuries has been unable to overcome.

With our wooden ships, metallic copper sheathing, if it were of the best kind, answered the purpose fairly well; but then the copper wasted so fast that inferior kinds and alloys were substituted to prevent the rapid loss, and, with the slowing down of the destruction of the copper, at once the trouble of fouling returned.

When a clean sheet of copper is exposed to the action of sea water, the first action is the formation of a thin film of cuprous oxide due to the action of dissolved oxygen in the water, and if oxygen be present, no corrosion of the copper takes place.

This cuprous oxide is then converted by the carbon dioxide and salts present in the sea water into carbonate and oxychloride, both of which are practically insoluble, and form a greenish blue deposit which peels off from the surface of the metal carrying with it any vegetable or animal germs and organisms which may have attached themselves to it, a process called "exfoliation." Sir Humphrey Davy, who first investigated this action, also found that the presence of even very small proportions of metals electro positive to it prevented this action and slowed down the wasting of the copper, but that this at once allowed fouling to take place.

If the purest copper also is not used, the scale of oxychloride and carbonate is more adherent; and setting up galvanic action with the still exposed metallic portions of the plate, after a short time causes it to be unevenly eaten away at these points.

When iron ships began to replace the wooden ones, as was only natural, attempts were made to utilise the metal which had before given relief; but it was quickly found that the effect of the galvanic action set up by the copper was fatal to the iron plates of the ship, and attempts were then made to sheathe the ship with copper plates in such a way that they should be insulated from the iron of the vessel; and this idea has been from time to time revived down to the present day, and, indeed, is in considerable use in some foreign services; but the difficulty of ensuring complete insulation, and the great risk of serious damage which must ensue to the iron of the hull if any injury happened to the insulating sheathing, makes it a most undesirable method if any other means can be adopted to fulfil the same purpose as that for which the copper is used.

Early in the history of iron ship building the idea was conceived of using coatings of paint, so prepared as to fulfil the same function as the copper plates had done; but from 1840, when the first paint of this kind was patented, down to the present day, when there are upwards of thirty two different compositions in the market, very little progress has been made in their manufacture, and the best of the present compounds cannot be relied upon for keeping a ship's bottom even fairly free from fouling for periods extending over nine months.

The idea which originally led to the present class of anti-fouling compositions was that the copper salts formed by the action of the sea water on the metallic sheathing owed a considerable portion of their value as anti-foulers to the poisonous action they exerted upon marine animal and vegetable growths; but, when an observer comes to study the natural history of these lower forms of animal life and vegetation, it is gradually forced upon one that it is only in the early stages of their growth—the germ period—that metallic poisons can affect them. Seaweeds do not take in the constituents they require for their growth by means of their roots, as is, to a certain extent, the case with ordinary plants, but absorb them by means of their pores from the water itself, the root only serving to attach them to the solid they choose for their resting place; and it is also well known that when once a marine plant which has passed the first stages of existence is dislodged or torn from its support, it cannot again attach itself to anything else, whilst most of the mineral poisons have little or no effect upon their life and growth.

In the same way we find that, with the animal life found on a ship's bottom, the under side is used to cling on with only, and not as an extractor of nourishment; and that, therefore, after the seeds and germs have once obtained a foothold on the side of the vessel, no amount of poison which can be put into a composition will have any effect upon them. Metallic poisons undoubtedly do exert an influence upon the germs in their earliest stages; but after that, they are perfectly useless as anti-foulers, and only imperil the plates of the vessel.

The germs of both kinds of growth are of necessity more abundant in the surface water near shore than in deep water, and, therefore, the period when the ship is in port is the time when the germs are most likely to make good their attachment, after which their further development is, unless other methods of getting rid of them are employed, merely a matter of time.

On examining the conditions under which a vessel is placed when coated with a composition which relies for its anti-fouling powers on metallic poisons only, we at once see the reasons which must make such a coating of little or no avail. In the composition we have drastic mineral poisons, probably salts of copper, mercury, or arsenic, which have been worked into a paint by admixture with varnishes of varying composition, and each particle of poison is protected from the action of the sea water by being entirely coated by this vehicle: that this must be so is evident, or the composition would not have sufficient cohesive power to stick on the ship. As a rule, care is taken to select fairly good varnishes, which will resist the action of sea water for, perhaps, two or three months, before they get sufficiently disintegrated to allow the sea water to dissolve any of the poison; whilst, even with the accidental or intentional use of inferior varnishes, three or four weeks will pass before any solution can take place, and any poison be liberated to attack the germs. A ship is dry docked, cleaned, and her anti-fouling composition having been put on, she goes probably into the basin to take in cargo. Here she is at rest, and, with no skin friction or other disturbing causes to prevent it, a slimy deposit of dirt from the water takes place, and this, as a rule, is rich in the ova and germs of all kinds of growth, whilst the poisons in her coating are locked up in their restraining varnish, and are rendered inactive at the only period during which they could be of any use. After a more or less protracted period, the ship puts to sea, and, the perishing of the varnish being aided by the friction of the water, the poisonous salts begin to dissolve or wash out of the composition; but the germs have already got a foothold, and with a vessel sweeping at a rate of, say 10 to 12 knots through the water, the amount of poison which can come in contact with their breathing and absorbing organs is evidently so infinitesimally minute that it would be impossible to imagine it having any effect whatever upon their growth. If the poison is soluble, it is at once washed away as it dissolves; if it is insoluble, then it is also washed away, but there is just a chance that a grain or two may become entangled in the organs of some of the forms of life, and cause them discomfort. As the surface varnish perishes, the impact of the water during the rapid passage of the vessel through the water quickly dissolves out or washes out the poisonous salts, and leaves a perished and porous, but still cohesive coating of resinous matter, which forms an admirable lodgment for anything which can cling to it; and by the time the vessel lays-to in foreign waters, teeming with every kind of life, the poison which would now again have been of some use is probably all washed away, and a fresh crop of germs are acquired, to be developed on the homeward voyage, and a "bad ship" is reported by the person who looks after her docking. It is evident that a poison, even if it had the power of killing animal and vegetable life in all stages, could only act with the vessel at rest, unless it were of so actively corrosive a nature as to burn off the roots and attachments of the life rooted to it; and if it did this, what would become of the protective composition and the plates of the vessel? Any poison so used must be under conditions in which it is very unlikely to be in a position to act when it might do good.

The lamentable failure of composition after composition of this kind has gradually reduced them in number to some ten or twelve at the present time, and in most cases it is low price alone which keeps them in the market.

The practical proof, given by experience, that poisons alone are unable to secure a clean bottom soon led many inquirers to the conviction that it was the exfoliation in the case of copper which had acted in giving fairly good results; and in many compositions the attempt has been made to provide a coating which shall slowly wash off, and, by losing its original surface, shall at the same time clear away germs and partly developed growths, and so expose a continually renewed surface; in this way keeping the bottom of the vessel free from life. There is no doubt that when this is successfully done, a most valuable composition will result, but the practical difficulties which beset this class of antifoulers must not be overlooked. In order to secure success, the composition must waste at a fairly uniform rate when the ship is at rest, and also when she is rushing through the water; and this is the more important in the case of Service vessels, as in many cases they spend a large percentage of their existence at anchor, or in the basins of our big dockyards. If a composition is made to waste so rapidly that it will keep a vessel clean for months in a basin, then you have a good composition *for that purpose*; but send the vessel to sea, and under conditions where you have water of a higher temperature, and the enormous friction caused by her passage through the water exerting its influence upon the composition, and you will find that the coating, which did its work well for six months at rest in the basin, will, in the course of one month under the altered conditions, be all washed away, and fouling will be set up. Noting this result, the manufacturer renders his composition more insoluble—less wasting—and so obtains a coating which, when the vessel is in motion, scales just fast enough to prevent fouling, and good results at once follow; the composition is then put on the same or other vessels, and they take a spell of rest in the basin, and bereft of the aid of the higher temperatures, and the friction of the water, the composition ceases to waste fast enough, and bad results at once have to be recorded.

There is no doubt that this is the true explanation of the wide discrepancies which are found between the compositions in the Navy and the Mercantile Marine. Take any of the big lines, their steamers are running at a fairly uniform rate of speed, and the periods of inaction are as short as the desire not to waste charge on the capital they represent can make them; and under these conditions, by varying the constituents in the varnishes used for anti-fouling purposes, it is fairly easy, given the necessary data, to so constitute a composition as to secure admirable results; but when you come to apply this same coating to an ironclad, running at various speeds, and as often at rest as in motion, then you at once find that the composition you before imagined to be all that could be desired fails just as lamentably as the tribe of anti-foulers which preceded it.

Another factor which is often overlooked, and which tends to give misleading results, is the action of brackish water, which, in many cases, seems to exert a special action in keeping the bottom of a vessel clean: the fresh water having a tendency to disagree with certain forms of marine growth, whilst the salt water is apparently equally unpalatable to the fresh water forms of fouling.

In most of the compositions now in use attempts are made to combine strongly poisonous substances with exfoliating and wasting coatings, and this is done by either using metallic soaps, the basis of which is, as a rule, copper, or else by charging a perishable and easily washed off varnish with poisonous salts, consisting as usual of compounds of either copper, mercury or arsenic, and in some cases all three.

As before pointed out, the presence of these substances does not exert any deterrent action upon the fouling, save perhaps when the vessel is at rest; but they exert undoubtedly an important influence upon the rate of exfoliation, as when the perishing of the varnish exposes them they dissolve, or are washed out, and in this way tend to disintegrate and clear away the surface more rapidly, an important and decidedly useful function, but one which might be more cheaply performed by substances other than high priced metallic poisons.

The use of metallic poisons of the character indicated throws an increased burden upon the protective composition, as, should the latter become abraded by friction of chain cables, barges alongside, or any other cause, the iron of the vessel will be attacked by the metallic salts, either present in the soluble form in the anti-fouling composition, or rendered so by the solvent action of the saline constituents of the sea water, the action of the metallic salts being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way, but copper is by far the most objectionable, from the fact that the salts formed by the action of the sea water upon some of the compounds used in the compositions are more soluble than the corresponding salts of mercury, and are, therefore, liable to be present in larger quantity, and so exert comparatively a much more injurious action on the plates.

All the time the ship is in motion, the wash of the sea water will prevent the metallic poisons doing the plates or the marine growths much harm, but there is one phase of this question which has been overlooked. In certain ports there is a fashion in compositions, and most of the homes of the Mercantile Marine have some pet local composition which is largely used at the particular port. If, now, many ships are lying in a basin, taking in and discharging cargo, and if the prevalent compositions contain soluble salts of copper, it is evident that a certain quantity will go into solution in the water, which often does not undergo frequent or rapid change, and under these conditions every ship in the basin will be exposed to the same danger, and wherever an abrasion has taken place in the protectives, there copper will be deposited on the iron, causing corrosion and destruction of the plates; and it must be remembered that when the vessel is next docked and coated no amount of scraping will remove the fine particles of copper deposited in the pitted and corroded portions of the plate, and so finely divided as to be invisible to the eye, but that it will remain and carry on its destructive work under the new coatings of protective.

It is a well recognised fact that, when a vessel coated with a copper compound has become corroded from failure of her protective, or from abrasion, even an entire change of composition does little or no good in stemming the tide of corrosion, until after some considerable period has elapsed, a result which is due to the same cause.

At the present time, 15 out of the 32 principal compositions rely upon copper in some form or other as the basis of their anti-fouling composition, and in one which has enjoyed considerable favour finely divided metallic copper itself is used, and should a vessel coated with it, after the varnishes had commenced to disintegrate, be moored alongside an iron ship by a chain cable, or even by a wet hawser, a big galvanic couple would be formed at the expense of serious damage to any exposed iron.

In the history of anti-fouling many attempts have been made to obtain highly glazed and glass like surfaces which it was hoped would withstand the action of sea water, and afford no lodgment to marine growths; but even glass itself is slowly acted upon by sea water, and, when once roughened on the surface, will foul, whilst the rigidity of such coatings, and the straining and cracking consequent on unequal expansion and contraction of the plates and their coating, offers a serious obstacle to any such scheme.

The protective composition is the important composition, and care must be taken to obtain the best in the market, as, if the protection is good, the plates remain uninjured even if fouling take place. The anti-fouling composition to be used with it must either be elastic, or have the same rate of contraction and expansion as the protective, and must—at any rate in the Navy—be chosen to suit the work to be done, such as contain soluble copper compounds being carefully rejected, whilst preference should be given to those which rely on exfoliation rather than mineral poisons. If a vessel is to remain at rest for a considerable period, an anti-fouling composition which exfoliates rapidly, and which also contains poisons known to act on germ life, must be used, the amount of such poison depending on the seasons and the waters in which the ship is to be; whilst if a vessel is to be continually running, then a slowly exfoliating composition must be employed, and a very small percentage of poison is all that is required, as skin friction and the comparative absence of the germs and spores in deep water will do the rest.

The question of colours is so closely allied to that of the various compositions and paints in use, that a few words on the nature of colour and the composition of the pigments employed will not be out of place.

All natural objects are distinguished by particular colours, and when we want to artificially imitate these colours we use strongly coloured bodies, called pigments.

When a beam of light falls on any substance, some of the coloured rays of which the beam is composed are absorbed and taken up by the substance, whilst the remaining rays are reflected back to the eye, and give the sensation of colour; for instance, a poppy looks red, because its petals have the power of absorbing all the rays, with the exception of the red rays, and these are reflected back to the eye.

A body which reflects all the rays of the spectrum in equal proportion, will appear of the same colour as the light that falls upon it, that is to say white. But the majority of bodies reflect some rays in larger proportion than others, and are therefore coloured, their colour being that which arises from the mixture of rays which they reflect.

A body reflecting no light would be perfectly black.

That this is true, may be seen by taking a source of light yielding only one kind of ray—called a monochromatic light; and all colours that have not the power of reflecting this particular ray appear black.

When light falls upon an opaque body, it is all either reflected or absorbed, but when it falls upon a transparent body, some of these rays are absorbed, whilst others pass through, and these are said to be transmitted.

A transparent body seen by transmitted light is coloured, if it is more transparent to some rays than to others, its colour being that which results from the mixture of the transmitted rays. Hence, a piece of blue glass appears blue, because it allows the blue rays to pass through.

The condition or state of division of a substance has a great influence upon its colour; for instance, gold is yellow by reflected light, brown in a state of fine powder, and when beaten out into very thin leaf, by transmitted light it is green; in a still finer state, as when precipitated from dilute solutions of gold, it appears blue or purple.

Temperature also, in many cases, affects the tints of colours, and often the colour itself: for instance, if scarlet iodide of mercury be heated, it becomes yellow.

But besides these influences, others of even greater importance are always at work, such as oxidation of the oil with which the colour is mixed, light, and the action of impure air; whilst in very many cases the colours used by the artist chemically act upon one another in the course of time, and entirely destroy the effect which he intended to convey.

In order to avoid as much as possible the deterioration of paintings from these and similar causes, it is of great importance that anyone using colours should have an idea of the composition and properties of the substances employed.

White lead or flake white is a basic carbonate of lead. The Dutch method of preparation is to expose gratings of lead (as pure as possible and free from silver, which, even in small quantities greatly impairs the good colour of white lead) to the action of the mixed vapours of vinegar (acetic acid) and carbon dioxide gas. The carbon dioxide is generated from a covering of spent tan and stable manure, the decomposition of which causes the requisite increase of temperature. The vapours of acetic acid attack the lead, and form a basic acetate, which, in its turn is converted into basic carbonate of lead, acetic acid being liberated, and this attacks a fresh portion of lead. After these actions have gone on for some time, the layers of basic carbonate are scraped off the gratings and ground to a fine powder. This rather clumsy process has been of late superseded by more rapid methods, in which tribasic acetate of lead formed by boiling an excess of litharge with acetic acid is decomposed by passing carbon dioxide through it. The white lead produced in this way has a crystalline structure and does not cover so well as that obtained by the Dutch method. White lead is very poisonous, and being a cumulative poison, painters and others often suffer from lead colic. In white lead manufactories the workmen drink water containing dilute sulphuric acid, so as to convert the lead into non poisonous sulphate of lead.

The great drawback to white lead as a pigment is that in foul air it gradually darkens. This is due to the fact that the air contains traces of sulphuretted hydrogen, which combines with the lead, forming sulphide of lead—a black compound.

Lead carbonate		Sulphuretted hydrogen		Lead sulphide		Carbon dioxide		Water.
$PbCO_3$	+	H_2S	=	PbS	+	CO_2	+	H_2O.

Pictures so blackened may be partially restored by washing the surface with a solution of hydrogen peroxide, which converts the black sulphide into white sulphate of lead.

Lead sulphide		Hydrogen peroxide		Lead sulphate		Water.
PbS	+	$4(H_2O_2)$	=	$PbSO_4$	+	$4(H_2O)$.

A little sulphide of lead or Berlin blue is sometimes added to the commercial white lead to give it a bluish tint.

Baryta, or permanent white, is sulphate of barium; it is deficient in body, but is of great use in fresco and siliceous painting. It is perfectly permanent under all conditions, and is not affected by sulphuretted hydrogen, since the sulphide of barium which might be formed is also white.

Zinc, or Chinese white, has now almost entirely taken the place of white lead in water colours, but is a little deficient in body for oils; this, however, is being remedied by slight alterations in the mode of preparation. The colour is not affected by sulphuretted hydrogen and is thoroughly permanent under all conditions. It is an oxide of zinc, and is the same body that we form when zinc is burnt in oxygen. It is now rapidly coming into favour, and for all important work will soon supersede white lead.

Most of the blacks consist of carbon in a very fine state of division.

Ivory black is practically animal charcoal, obtained by carbonising ivory cuttings.

Vine black is a vegetable charcoal, obtained from the twigs of vines, and is given a blue black tint by mixing it with some Prussian blue.

Lamp black is a very finely divided soot, made by burning resinous oils in an insufficient quantity of air, and condensing the smoke.

Indian ink and Chinese ink consist of lamp black, mixed with gum, shellac, a little borax and water.

All these blacks are good and permanent, and may be mixed with other pigments without fear; it is better, however, not to mix ivory black with vegetable colours.

Mineral black (which is very little used) is black oxide of manganese; it does fairly well in oils, but always has a brown tint.

We now come to the reds, and these are of two kinds:—(1) Mineral reds, like vermilion, and (2) Organic reds, like carmine, &c.

Mineral Reds.—Indian red, Venetian red, light red, chiefly consist of peroxide of iron, with an admixture of basic sulphates of iron. They are prepared by heating sulphate of iron (the green vitriol of commerce) with a small trace of nitric acid.

$$\overset{\text{Ferrous sulphate}}{2(FeSO_4)} = \overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Sulphur trioxide.}}{SO_3}.$$

The peroxide is permanent under all ordinary conditions, but it must be carefully freed from all traces of acid before being applied as a paint to the surface of iron. It is much used in protective coating for ships.

Red ochre is a soft variety of the iron ore hæmatite (Fe_2O_3) containing a little clay.

Red lead or minium (Pb_3O_4) is a mixture of monoxide of lead with peroxide (PbO_2). It can be prepared by carefully heating litharge or monoxide of lead, in a current of air to a temperature of 316° C. The litharge absorbs oxygen and is converted into red lead. The finest coloured minium, or Paris red, is formed from carbonate of lead in the same way.

Red lead, although much used, is very unsuitable, as it is open to all the objections of white lead, and also when mixed with oils forms with them a kind of soap, which causes the colour to lose its opacity.

When linseed oil is boiled for some time with oxide of lead, it forms and dissolves some of this lead soap, and acquires the property of rapidly drying. Such oil is technically called "dryers," and is much used to mix with oil paints to cause them to quickly dry; but as it contains lead, all colours mixed with it are liable to darken in the presence of sulphuretted hydrogen.

Vermilion is the most brilliant of the mineral reds. It is a sulphide of mercury (HgS) and is found native as cinnabar. It may be artificially prepared by precipitating the black sulphide of mercury from a solution of mercuric chloride. This black sulphide on being sublimed and ground up fine, changes to the red variety without altering its composition. The most brilliant colour is obtained by the wet process, which consists of triturating mercury and sulphur together for some hours, and treating the black product formed with a warm solution of caustic potash and water. The colour is not destroyed by any single acid or alkali. When used as a water colour it is apt to turn black in sunlight.

Chrome red. This pigment is a basic chromate of lead, known also as Austrian cinnabar ($PbCrO_4 + PbH_2O_2$). It is best prepared by fusing the nitrates of sodium and potassium together at a low red heat, and adding gradually yellow chromate of lead. After cooling, the insoluble chrome red is well washed and dried.

Organic Reds.—Madder lake, rose madder, carmine madder, is made by treating madder, the root of the "*Rubia Tinctorum*," which has been previously washed with water, with a boiling solution of alum, filtering the red liquid, and adding some carbonate of soda, which causes a red precipitate of the colouring matter and alumina, which is the madder lake.

Carmine derives its colour from cochineal which contains carminic acid, and this is split up by acids into carmine red and glucose.

The common carmine is obtained by treating an aluminous solution of cochineal with carbonate of soda, the lake being precipitated.

Crimson lake contains more aluminous base than carmine, and consequently has not such a fine colour.

Scarlet lake is crimson lake with an admixture of vermilion.

The Yellows.—Aureolin yellow is made by warming a solution of cobalt with potassic nitrite in presence of acetic acid, when the yellow is precipitated; it is a rich colour, and mixes well with other pigments.

Cadmium yellow is a sulphide of cadmium, and is a very stable and valuable colour, being unaffected by sulphuretted hydrogen. It is best prepared by precipitating a solution of sulphate of cadmium with sulphide of sodium, and thoroughly washing and drying the precipitate. Lemon chrome or baryta yellow is chromate of barium; it is difficult to prepare, and the stability and beauty of colour depend on the method of manufacture. The colour is very permanent.

Chrome yellow is a neutral chromate of lead and can be obtained by adding chromate of potash to a solution of lead acetate. The pigments known as chrome orange are mixtures of chrome yellow and the basic chromate, or chrome red, and are prepared by boiling chrome yellow with milk of lime.

The ochres are native earths consisting chiefly of alumina and silica coloured by sesquioxide of iron. They are very permanent and can be used with great safety. When heated they become brown, and are then called sienna.

Gamboge is a gum resin which exudes from the young shoots of the gokathu tree in Ceylon and Siam.

Yellow carmine and yellow lake are prepared from quercitrin, a colouring matter existing in the bark of the quercitron. It is precipitated by means of alum.

Indian yellow or purree consists of an organic compound of magnesia, and is obtained from the urine of the camel.

The Greens.—Among the many pigments that owe their green colour essentially to copper, the following are important:—

Brunswick green consists of oxychloride of copper ($CuCl_2 3CuO 4H_2O$), formed by boiling sulphate of copper with chloride of lime.

Bremen green is hydrated oxide of copper, obtained in various hues by mixing with barium sulphate.

Casselmann's green. A basic compound formed by mixing together boiling solutions of copper sulphate and an alkaline acetate. This salt is, next to the arsenic compounds, the finest of all the colours obtained from copper.

Mineral green or Scheele's green, is arsenite of copper ($CuHAsO_3$).

Schweinfurt green or emerald green. This is the most beautiful, but also most poisonous of all the copper pigments. It is really an aceto-arsenite of copper and may be made by adding sodic acetate and arsenious acid to a solution of sulphate of copper. It is a well known fact that paper hangings containing this pigment and pasted on damp walls, cause the inmates of the rooms to suffer from headaches, due probably to volatile arsenical vapours being formed.

Verdigris is a subacetate of copper. As a water colour it is very unstable.

Chrome green, viridian green, are oxides of chromium, and are prepared by adding sodic hydrate or sodic carbonate to a solution of chromic chloride. They have poor body, but are themselves unchangeable, and do not affect other colours with which they may be mixed.

Terre vert is a very permanent green, consisting of an oxide of iron and silicate of iron.

Other greens are compounded from yellows and blues; if mixtures (such *e.g.*, as Prussian blue, mixed with raw or burnt sienna or Vandyke brown) be exposed to light, the green colour gives place to brown, on account of the Prussian blue fading. If the faded colour be then kept for some time in the dark, the colour returns.

The Blues.—Ultramarine. This is a double silicate of alumina and soda, and contains sulphur in the form of sulphide, but no definite formula has been found for it. It occurs native as "lapis lazuli." The commercial product is obtained by heating together soda, clay, sulphur and charcoal in various proportions. It is first white, but quickly turns green (green ultramarine), and when this is heated with sulphur in presence of air it becomes blue without change of composition. Ultramarine is unacted on by alkalis, but is readily decomposed by acids with evolution of sulphuretted hydrogen.

Cobalt and smalt blues are exceedingly permanent under all ordinary conditions. They are prepared by dissolving cobaltous oxide in a fused acid silicate, which yields a glass of magnificent blue colour, which is ground to a fine powder.

Prussian blue is ferrocyanide of iron; it is made by adding a persalt of iron to potassic ferrocyanide, when Prussian blue is precipitated. It is readily destroyed by alkalis. The pigment is soluble in oxalic acid and molybdic acid.

Indigo is the blue colouring matter obtained from several species of *indigofera*. The leaves are macerated in water, when they undergo oxidation, forming a yellow solution, which, on exposure to the air, deposits indigo in the form of a dark blue powder. The pigment is soluble in Nordhausen sulphuric acid, forming a deep blue solution. For dyeing purposes the cloth is dipped in a vat containing 1 part of indigo, 2 parts of ferrous sulphate, 3 parts of slaked lime, to about 200 parts of water. On exposure to air the cloth becomes permanently blue by the deposition of insoluble blue indigo. Indigo has also been prepared synthetically.

The Browns.—Raw and burnt umber consist of a native ore of iron, containing a little manganese. The pigments are permanent.

Sepia is extracted from cuttlefish, and consists of carbonaceous matter and animal gelatine.

Madder brown is extracted from the madder root, and is very apt to fade, whilst Vandyke brown and the brown ochres are oxides of iron, and are quite permanent.

From a series of experiments lately made on the action of light on water colours, the following notes may be of interest.*

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* Report of the action of Light on Water Colours, by Russell and Abney.

Paper painted with simple colours and mixtures were exposed to light under different conditions, with the following results.

Mineral colours are far more stable than vegetable colours.

The presence of moisture and oxygen are in most cases essential for a change to be effected, even in the vegetable colours. It may be said that every pigment is permanent when exposed to light "in vacuo"

The effect of light on a mixture of colours which have no direct chemical action on one another, is that the unstable colour disappears, and leaves the stable colours unaltered appreciably.

Experiments also show that the rays which produce by far the greatest change in a pigment, are the blue and violet components of white light, and that these for equal illumination, predominate in light from the sky, whilst they are less in sunlight and in diffused cloud light, and are present in comparatively small proportion in the artificial light usually employed in lighting a room or gallery.

Experiments have also shown that about a century of exposure would have to be given to water colour drawings in galleries lighted as are those at South Kensington, before any very marked deterioration would be visible in them, if painted with any but the more fugitive colours; and that when the illumination is of the same quality as that of gaslight, or of the electric glowlight, rendered normally incandescent, and of the same intensity as that employed in those galleries, an exposure to be reckoned by thousands of years would be necessary to produce the same results.

QUESTIONS.

1. Point out the difference between physical and chemical change and illustrate your answers by examples.
2. To which kind of change do the following phenomena belong:
    - (*a*) Conversion of water into ice.
    - (*b*) The rusting of iron.
    - (*c*) The burning of a jet of coal gas.
3. Why do solids seldom react upon each other? Enumerate some of the causes which tend to set up chemical action, and give examples.
4. Why are iron, sulphur and oxygen called elements?
5. State the leading characteristics which serve to distinguish between a chemical compound and a mechanical mixture, and illustrate your answer by examples.
6. What reasons have we for saying that water is a chemical compound? How would you prepare oxygen and hydrogen, respectively, from steam?
7. Give two methods for the preparation of hydrogen. What precautions must be observed in preparing and collecting it?
8. Enumerate some of the more characteristic properties of hydrogen.
9. Describe the effect of hydrogen on sound.
10. Explain fully what is meant by the density of a gas.
11. What precautions must be observed in comparing the weights of equal volumes of gases?
12. What is meant by normal or standard temperature and pressure?
13. If the pressure remain constant, to what temperature must the air in a vessel be heated so that half may be expelled?
14. A room contains 560 cubic feet of air at 5° C. and 762 m.m. How much air will be driven out at 12° C. and 750 m.m?
15. Describe fully the grounds for believing hydrogen to be the vapour of a metal.
16. Give examples to show that hydrogen in combination can, in some cases, be replaced by metals and also that, under certain conditions, metals can be turned out from their compounds and be replaced by hydrogen.
17. Under what circumstances can oxygen be condensed to a liquid?
18. Give two methods for the preparation of oxygen from water. How is oxygen commonly prepared for experimental purposes? What products are formed when phosphorus, carbon, sulphur, zinc and iron, respectively, are burnt in oxygen?
19. How is the solution of oxygen in water affected by change of temperature? What important functions does dissolved oxygen perform?

20. Into what classes can "oxides" be divided? Illustrate your answer by examples.

21. How would you define the term "combustion"? Describe an experiment to show that the terms "combustible" and "supporter of combustion" are purely relative.

22. What is "slow combustion"? Give examples.

23. A cubic inch of wood in burning gives out x units of heat. How much heat would be evolved if it had been allowed to slowly decay? Give a short description of the process taking place during "respiration."

24. Give examples of cases in which natural oxidation (*i.e.* slow combustion) gives rise to sufficient heat to induce rapid combustion.

25. A piece of freshly heated platinum foil when held in a stream of mixed coal gas and air becomes red hot, and continues to glow all the time it is held in the mixture. Explain fully the action which is taking place.

26. Certain compounds contain oxygen so loosely held in combination that they will give it up to any easily oxidisable bodies. What are such compounds called, and what is their use in explosives?

27. Describe the preparation of ozone. How can ozone be detected?

28. Why do we say that ozone is an allotropic modification of oxygen?

29. Define the terms "Allotropism" and "Isomerism," and give examples.

30. How can ozone be converted into oxygen? Describe the experimental proofs that the density of ozone is 24 on the hydrogen scale.

31. Show how you could prove that the proportions in which oxygen and hydrogen exist in water are by weight as 8 to 1.

32. Define the terms "molecule" and "atom."

33. Write the symbols for sulphur, silicon, silver; and write the formulæ for sulphuric acid and zinc sulphate, and the equation for the action of hydrochloric on chalk.

34. What is the "atomic weight" of an element?

35. How could the atomic weights of chlorine, cobalt, and iron respectively be determined?

36. The molecular weight of carbon dioxide is 44; what is its density on the hydrogen scale?

37. Show how the "specific heat" of an element may be used as a guide in determining its atomic weight.

38. What do we mean by the "equivalent weight" of an element? 65 grams of zinc will expel 2 grams of hydrogen from sulphuric acid. What is the equivalent weight of zinc?

39. How can it be proved that the molecule of hydrogen contains two atoms?

40. The density of a gas on the hydrogen scale is 22. What will be the weight of 22.32 liters of this gas at normal temperature and pressure?

41. How much zinc and how much sulphuric acid must be employed to generate sufficient hydrogen to fill a balloon with capacity of 1,250 liters? A.W. $Zn=65$; $S=32$; $O=16$.

42. The molecular weight of nitrogen is 28. What will be the weight of 500 liters of the gas?

43. Write out the formulæ for the chlorides, nitrates, sulphates and phosphates of potassium, calcium, bismuth respectively.

44. How can we explain the fact that sulphur acts as hexad in sulphur trioxide and tetrad in sulphur dioxide?

45. Describe how the heat evolved by the action of zinc on dilute sulphuric acid can be converted into electricity.

46. By what experiments could you prove that when a plate of zinc and a plate of copper are placed in dilute sulphuric acid and are in metallic contact, a current of galvanic electricity is produced?

47. How do you explain the rapid falling off of the current in a simple voltaic combination?

48. Describe and explain the methods employed in the following cells to prevent this falling off (*a*) Daniell, (*b*) Varley-Daniell, (*c*) Menotti, (*d*) Leclanché, (*e*) Grove?

49. Why is Daniell's battery not used for firing fuses? What advantages has the Leclanché battery?

50. For what purpose is the Menotti cell mostly used?

51. How is the internal resistance of a Leclanché battery intended for firing purposes made as low as possible?

52. Explain the chemical actions taking place in a "bichromate cell" and illustrate your answers by equations. Why must sulphuric acid be used in excess in charging this form of cell?

53. Describe what happens when a current is passed through acidulated water using lead electrodes?

54. Explain fully the action and changes taking place in a secondary battery.

55. Explain the terms "electrolysis," "electrolyte," and "electrode." Describe what happens when a galvanic current is passed through a solution of sodic sulphate?

56. The same current is passed through 3 cells containing respectively—sodic chloride, copper sulphate and silver nitrate; explain the decomposition taking place in each cell. What ratio by weight do the copper and silver deposited bear to each other and to the zinc used up in each cell of the battery?

57. Explain the process of electro plating.

58. What is the use of zinc protectors on ships' bottoms?

59. A pound of water at 80° C. is mixed with 1lb of ice at 0° C. What will be the temperature of the two pounds of water formed?

60. Define the terms "latent heat," "thermal unit" and "boiling point." Upon what does the boiling point of a liquid depend? Illustrate your answer by the description of experiments.

61. How can the boiling point of water be raised above 100° C.?

62. On what conditions does the rate of solubility of a gas in water depend? A pint of water will dissolve a pint of carbon dioxide gas at 15° C. and 760 m.m. pressure; what volume of gas will be dissolved if the pressure be increased to 1140 m.m.?

63. Why does a solid dissolve more quickly if the solvent be constantly agitated?

64. Explain the freezing of water by the rapid solution of ammonic nitrate. What is meant by "water of crystallisation" and "water of hydration"?

65. What is the purest form of natural water? What classes of impurities are found in rain, spring and river water respectively?

66. To what is hardness in water due? What is meant by the terms "a degree of hardness," "temporary hardness," and "permanent hardness"? Describe and explain Clarke's process for softening water.

67. How is boiler deposit formed? What constituent of boiler deposit tends to render the scale hard? How does the composition of the deposit in land boilers differ from the deposit in marine boilers?

68. Explain the action of sodic carbonate as an "anti-incrustator." Sal-ammoniac is sometimes used for the prevention of incrustation in steam boilers; what is its action, and why would it be no use for boilers using sea water?

69. Why should tallow and other animal and vegetable fats and oils not be employed as anti-incrustators? What kind of oil might be used for this purpose with advantage?

70. Explain why magnesium is found as magnesic hydrate in boiler deposits. How does the decomposition of magnesic chloride in steam boilers affect the corrosion of boiler plates?

71. Why is shallow well water especially liable to organic contamination?

72. Give two rough methods by which stream water charged with vegetable impurities may be rendered fairly fit for drinking. Why are rough tests of the fitness of a water for drinking purposes as a rule misleading?

73. How can peroxide of hydrogen be prepared? Give an equation for its formation.

74. Peroxide of hydrogen is brought in contact with (*a*) litmus solution, (*b*) silver oxide, (*c*) finely powdered platinum, (*d*) black oxide of manganese, respectively. What happens in each case?

75. By what tests can peroxide of hydrogen be detected in solution?

76. How is marsh gas formed?

77. What weight of carbon will be contained in 22.32 liters of marsh gas?

78. Explain the terms "fire damp" and "choke damp." On what principle is the safety lamp constructed?

79. In what proportions do marsh gas and air form the most explosive mixture?

80. How does ethylene or olefiant gas differ from methane or marsh gas? Describe an experiment which proves the presence of carbon in ethylene.

81. How can marsh gas and olefiant gas be prepared? Illustrate your answer by equations.

82. Give a brief description of the manufacture of coal gas and point out the use of the "hydraulic main," "atmospheric condensers," "scrubbers" and "purifiers,"

83. What are the "secondary products" of the manufacture of coal gas, and how are some of them utilised? Why must coal gas be purified from sulphur compounds?

84. Describe the structure of a candle flame. Why is the flame of a Bunsen burner non-luminous?

85. If a glass globe be used with a batswing or fishtail burner, what should be its form?

86. Why does an exposed flame give but little light in windy weather?

87. When an Argand burner is lighted it gives a smoky flame until the chimney is put on. Why is this?

88. Explain the principle of the Albo-carbon light.

89. What is the construction of incandescent gas lamps, and how do they differ from regenerative burners?

90. Explain the cause of the increase in luminosity obtained with regenerative burners.

91. Describe the preparation of carbon dioxide, and illustrate your method by an equation.

92. By what tests would you distinguish carbon dioxide from other gases? Give the characteristic properties of carbon dioxide and describe experiments to illustrate them.

93. How is carbon dioxide formed in Nature? What volume of carbon dioxide is formed by the combustion of 12 grams of carbon in oxygen? 16 liters of oxygen are converted into carbon dioxide. What volume will the gas occupy?

94. Describe and explain the preparation of carbon monoxide. Under what conditions is this gas formed during combustion?

95. How can you distinguish carbon monoxide from carbon dioxide and from hydrogen respectively?

96. Ten cubic feet of carbon dioxide are passed over red hot charcoal. What volume of carbon monoxide will be produced?

97. Explain the action taking place in a clear coke fire.

98. What is the composition of wood, and upon what does its value as fuel depend?

99. What advantages are gained by carbonising wood before using it as fuel? Describe the preparation of wood charcoal. What effect has the temperature and rate of burning upon the yield obtained from the charcoal heap? Why do we say that all our fuels are of vegetable origin?

100. What advantages are gained by converting coal into coke for metallurgical purposes?

101. How does "oven coke" differ from "gas coke"? What are the relative values of coke and coal as fuel?

102. Discuss the advantages to be derived from the use of "liquid fuel" in marine boilers.

103. Why would crude petroleum, as obtained from the wells, be unfit for use on board ship?

104. Into what two classes may the liquid fuels be divided?

105. Describe a method by which "heavy tar oil" may be burnt for heating or illuminating purposes.

106. How do coal gas, water gas, and generator gas differ in composition?

107. Describe the method used by Favre and Silbermann to determine the heat of combustion of various substances.

108. What is meant by a "thermal unit"? Express the latent heat of steam in thermal units on both °C. and °F. scales.

109. Calculate the thermal value of marsh gas on the assumption that it contains 75 per cent. carbon and 25 per cent. hydrogen. Why does the value so obtained differ from the value given by experiment? Give a formula for the calculation of the evaporative power of a fuel containing carbon, oxygen, and hydrogen.

110. Why does the calculated evaporative value of a fuel approach more nearly the actual value in the case of coke than with coal?

111. How does "calorific intensity" differ from "thermal value"? Describe two methods for the preparation of nitrogen from air.

112. 100 c.c. of *pure* nitrogen are required. Describe how you would prepare it, and give the quantity of material you would have to use.

113. How can nitrogen be distinguished from carbon dioxide?

114. What is the result of warming together a mixture of lime and sal-ammoniac?

115. A mixture of air and ammonia gas is given. How could you roughly determine the volume of ammonia present?

116. What is the composition of the fumes formed when ammonia gas comes in contact with hydrochloric acid gas? Why do we call the compounds formed by neutralising acids with ammonia, ammonium salts?

117. Describe the preparation and properties of nitrogen monoxide. Why is it often called "laughing gas"?

118. Why is nitrogen monoxide called an "endothermic" compound? How has its composition been determined?

119. Describe the preparation and physical properties of nitrogen dioxide. How can nitrogen dioxide be used as a test to distinguish between oxygen and nitrogen monoxide? How could you convert nitrogen dioxide into trioxide?

120. What compound is formed when nitrogen trioxide is dissolved in ice cold water?

121. Give an equation for the preparation of nitrogen tetroxide. What happens when this gas is dissolved in water?

122. How does nitrogen pentoxide differ from the other oxides of nitrogen?

123. How is nitric acid prepared? Explain your process by an equation. What are the characteristic properties of nitric acid? Why do we call it an oxidising agent?

124. What is the specific gravity of the strongest form of nitric acid? At what strength can you redistil it without decomposition.

125. How is nitric acid formed in Nature? Explain a process by which saltpetre can be artificially prepared. By what tests can a nitrate be recognised.

126. Describe experimental evidence to prove that the pressure exerted by the atmosphere is 15 lb. on the square inch.

127. How can the barometer be used as a measure of altitude. Explain fully the means by which Lavoisier demonstrated that the air contained oxygen and nitrogen?

128. What is the percentage of oxygen in air by volume and by weight?

129. Give a description of the eudiometric analysis of air. How is the composition of air by weight determined?

130. 3½ million tons of oxygen are daily abstracted from the atmosphere and replaced by CO_2. Explain why it is that the composition of the air does not alter.

131. Into what classes may "local" impurities in air be divided? Give examples. What important actions depend upon the organic matter present in air?

132. Why is ozone rarely, if ever, found in the air of towns?

133. How is it that the carbon dioxide formed during combustion and respiration in cities does not accumulate there?

134. Why is it practically impossible to render a room air tight? What important effect has this upon health.

135. Gases diffuse and intermingle at a rate which depends upon their density. Why should the air in a room diffuse out through the walls, etc., whilst fresh air diffuses in?

136. Describe an experiment to show that air which has once been breathed, is unfit for respiration.

137. Discuss the effect of various illuminants on the air of a room. Why is good ventilation of especial importance on board a warship.

138. Describe experiments to prove that combustion may be so rapid as to produce explosion.

139. To what causes is explosion due? Define the term explosion.

140. Into what classes can explosives be divided? Give an example of each.

141. How is saltpetre found in Nature? Explain the probable method of formation of the Indian nitre beds.

142. Describe and fully explain the preparation of potassic nitrate from Chili saltpetre.

143. Describe the method employed in purifying "grough saltpetre" at Waltham Abbey.

144. Explain the chemical decomposition taking place when KNO_3 is heated (*a*) to a moderate temperature, (*b*) to a very high temperature.

145. Why does charcoal deflagrate when saltpetre is fused upon it?

146. Explain why a charcoal made at 320° C. is more inflammable than a specimen prepared at 560° C. Why is cocoa powder brown instead of black?

147. How is charcoal for gunpowder prepared?

148. Why is sulphur said to be "dimorphous"? What is the crystalline form of native sulphur and how can it be artificially prepared?

149. Describe the preparation of prismatic and plastic sulphur. What changes do these forms undergo when kept? Describe the changes which sulphur undergoes between the temperatures of 0° C. and 1,000° C.

150. Which form of sulphur is always employed in the manufacture of gunpowder? What objection can be urged against the use of "flowers of sulphur"?

151. Describe the manufacture of R.F.G. powder.

152. What are the chief points which must govern the selection of the powder for any particular class of gun? Why would the class of powder used in a fieldpiece be totally unsuited for a 6-inch gun?

153. How would you distinguish between "black prism," "E.X.E.," and "S.B.C.," even if unable to see the colour?

154. What led to the introduction of prism powder? Discuss the properties of the powders which give high muzzle velocities with low pressure.

155. Briefly describe the methods used to determine the pressure and muzzle velocity given by powders.

156. Give the formula for cellulose and with an equation show the change which it undergoes when acted upon by the strongest nitric acid.

157. Why is strong sulphuric acid used in the manufacture of guncotton? Give the proportions by weight and by volume of the mixed acids used for this purpose. What ought their respective specific gravities to be?

158. Give a short account of the manufacture of guncotton as at present practised in the Government factories.

159. Given a sample of guncotton, how would you test it for (*a*) free acid, (*b*) collodion cotton, (*c*) unconverted cotton?

160. Why is the presence of a large percentage of collodion cotton in guncotton to be avoided?

161. How should guncotton be fired to develop the maximum explosive force?

162. Explain why guncotton is not used as a propellant in large guns.

163. Why is guncotton one of the safest explosives?

164. Why would the substitution of ammonic nitrate for potassic nitrate in gunpowder render it practically smokeless? What objection is there to the use of ammonic nitrate?

165. What methods have been employed to render guncotton sufficiently "tame" for use in small arm ammunition?

166. From what source is glycerin obtained? Give its formula.

167. Describe the preparation of nitro-glycerin, and illustrate your method by an equation.

168. Why is "dynamite" a better and more convenient explosive for blasting purposes than nitro-glycerin?

169. Explain the theoretical grounds for considering blasting gelatine a more perfect explosive than guncotton. What is the composition of this explosive?

170. How is picric acid prepared? How does the composition of picric acid differ from guncotton and nitro-glycerin? Write a formula for picric acid, and for ammonium picrate.

171. What is the principle of the "Sprengel explosives"?

172. Describe the preparation of mercuric fulminate, and write an equation illustrating its decomposition.

173. What compounds does sulphur form with hydrogen? Describe an experiment to show that sulphur and hydrogen will combine directly.

174. Give an equation for the preparation of sulphuretted hydrogen: what are the characteristic properties of the gas? How has its composition been determined.

175. A pint of oxygen is completely converted into sulphur dioxide by burning sulphur in it. What will be the volume of the resulting gas?

176. How would you prepare and collect pure sulphur dioxide? Explain fully the bleaching action of sulphur dioxide, and show how sulphur dioxide may be converted into sulphur trioxide.

177. Give a short description of the manufacture of sulphuric acid.

178. What part do the oxides of nitrogen play in the manufacture of sulphuric acid?

179. What is the specific gravity of "B. O. V." acid? How is "B. O. V." acid converted into oil of vitriol? What are the properties of sulphuric acid?

180. Describe some of the most characteristic properties of chlorine.

181. Describe two methods for the preparation of chlorine, and give equations in explanation of the actions which take place.

182. On what does the bleaching action of chlorine depend?

183. What is formed when bodies containing hydrogen are burnt in chlorine?

184. Under what conditions do chlorine and hydrogen unite to form hydrochloric acid? Describe the preparation and properties of hydrochloric acid gas. How can chlorides be detected in a solution?

185. What is the composition of bleaching powder and how is it prepared?

186. Explain fully the action which takes place when chlorine gas is passed into a cold dilute solution of potassic hydrate. What change takes place when this solution is boiled? If chlorine is passed into a hot concentrated solution of potassic hydrate, what reaction takes place?

187. Why is potassic chlorate called an "endothermic" compound? What bearing has this on its use as a source of oxygen?

188. By what tests could you distinguish a chlorate from a chloride? What are the chief sources of iodine and bromine; describe their preparation?

189. How has fluorine been isolated? What are the chief properties of hydrofluoric acid?

190. What are the chief native compounds of phosphorus? How is phosphorus prepared? Explain your process by equation.

191. What are the characteristic properties of phosphorus, and how does amorphous phosphorus differ from the ordinary variety? How is amorphous phosphorus prepared from the ordinary variety?

192. How many oxides of phosphorus are there? How would you obtain metaphosphoric, pyrophosphoric and orthophosphoric acids respectively from phosphorus pentoxide?

193. Give an equation for the preparation of phosphuretted hydrogen. Why is it spontaneously inflammable in air? How could you deprive it of this property? What is "Holmes' light"?

194. How is silicon obtained? Describe the preparation of silicic acid. What is glass? Mention some of the natural forms of silica.

195. What special properties distinguish the metals from the non metals? What elements may be classed with either group?

196. Why are metals rarely found free in Nature, and with what other elements are they generally associated?

197. State the general methods used in metallurgical processes, and distinguish clearly between "reducing" and "oxidising actions"?

198. What is understood by the terms "ductility," "tenacity," "specific gravity," "conductivity for heat and electricity" of metals? Give a list for each in their relative order.

199. How is potassium prepared, and what precautions must be taken in its manufacture?

200. What happens when potassium is thrown on to water, and how could you detect its presence in solution?

201. What is "bay salt"? How is this substance purified?

202. Two grams of metallic sodium are thrown on to water; what weight of caustic soda is formed, and what weight of pure sulphuric acid must be added to neutralise the solution?

203. Write a short account of the manufacture of soda crystals from common salt?

204. One gram of soda ash acted on with sulphuric acid yielded 157 c.c. of carbon dioxide gas at standard temperature and pressure; what percentage of carbonate did it contain?

205. Given a sample of ordinary sodium carbonate, how could you prepare from it, bicarbonate of soda, and caustic soda?

206. What compounds of barium and strontium are used in the arts, and to what purpose?

207. Give the name and composition of the chief forms of calcium found in Nature?

208. Which native compound of calcium is principally used for the formation of its salts, and why?

209. How is quicklime prepared, and how converted into slaked lime? How do impurities affect the result?

210. Carbon dioxide is bubbled through a solution of lime water; explain what happens, also state what further changes may take place.

211. Account for the hardness of some waters, and explain how it may sometimes be remedied?

212. What is plaster of Paris? How is it made, and what precautions must be taken in its preparations? What properties render it valuable for taking casts?

213. What happens when a platinum wire moistened with a solution containing calcium is heated in the non luminous flame of a Bunsen burner? What differences are noted when solutions of barium or strontium salts are used?

214. Describe what is observed when a beam of white light is examined by means of a prism?

215. Describe the method of applying the spectroscope to the study of (1) solids, (2) gases. What conditions of the substances modify the effects observed?

216. Explain what is meant by the so called Fraunhofer's lines.

217. How can the spectra of various metals be obtained, and what evidence is there for supposing that iron exists in the atmosphere of the sun?

218 A Bunsen flame coloured with sodium vapour gives two bright yellow lines; how can this experiment be altered to obtain a reversion of this phenomena?

219. What are the sources of magnesium in Nature, and to what uses is the metal put?

220. Given the metal magnesium, how would you prepare the sulphate, oxide, carbonate, and nitrate?

221. Give the composition of dolomite, Epsom salts, magnesite and meerschaum.

222. To what uses is the metal aluminium put, and what chemical and physical properties adapt it for such?

223. How would you prove that clay contains aluminium?

224. What is the composition of aluminium bronze; what advantages does it possess?

225. Name several precious stones which are constituted principally of alumina.

226. Describe the class of bodies called the alums. How is ammonia alum prepared?

227. Define the terms "mordant" and "lakes."

228. What is the action on the metal aluminium of (1) acids, (2) alkalis?

229. State the composition of the principal ores of manganese?

230. What is Condy's fluid, and to what purposes is it put?

231. What compounds of chromium are used in the Arts?

232. What is smalt? What special properties render it of value as a pigment?
233. To what protective purposes is the metal nickel put? Give the composition of German silver.
234. Enumerate the principal iron ores used for obtaining the metal in large quantities.
235. Describe the manufacture of cast iron from clay ironstone.
236. What is slag? Why is limestone added with the fuel?
237. How do white and grey pig iron differ in composition and qualities? Under what circumstances does a furnace yield the one or the other?
238. What chemical changes take place in the processes of "refining" and "puddling"?
239. Why cannot the iron be purified beyond a certain extent in the open hearth or refinery process?
240. Describe briefly the puddling process.
241. How is the iron as removed from the puddling furnace freed from traces of slag and rendered homogeneous?
242. Distinguish between "rough" and "merchant" iron.
243. What do you understand by the "acid" and "basic" linings of a furnace? How is the quality of the metal affected in either case?
244. Explain the terms "cold shortness" and "red shortness" as applied to iron.
245. What conditions sometimes change the fibrous structure of wrought iron and render it brittle?
246. How do cast iron. wrought iron and steel, vary in chemical composition and properties?
247. Describe (1) the ordinary method of making steel, (2) that known as Bessemer's method.
248. How can the physical conditions of steel be rapidly altered to suit the various applications?
249. What is spiegeleisen? In what processes is it used?
250. State the action of cast iron, wrought iron and steel, under the hammer when (1) cold, (2) hot.
251. Describe the principal and advantages of the Siemens-Martin process.
252. What is the effect of extreme pressure on steel during solidification?
253. Describe the manufacture and action of armour plates.
254. What effect on the quality of the metal have the following:—manganese, phosphorus, nickel and sulphur?
255. Describe the various processes in use for obtaining zinc from its ores.
256. Give the properties of zinc and its commercial uses. What is meant by galvanized iron?
257. A piece of zinc is soldered on to a bar of bright iron and placed in water. Explain why the steel does not rust? What happens to the zinc?
258. What metal is generally found associated with zinc? How are they separated?
259. What is the chief ore of antimony? How is the metal obtained?
260. What alloys of antimony are useful? What characteristic change does antimony produce?

261. Describe the chlorides of antimony. What happens when they are added to water?
262. Give the composition and uses of fusible metal.
263. What action has nitric acid on antimony, bismuth and tin?
264. What processes has tinstone to undergo for the extraction of the metal?
265. For what purposes is it necessary to use pure tin and how is it obtained perfectly pure?
266. Describe the compounds of tin with oxygen?
267. How is copper obtained from copper pyrites?
268. What is the action of moist air on metallic copper?
269. What happens when a sheet of bright steel is placed in a solution of copper sulphate?
270. What are the characteristic properties of the salts of copper?
271. Why is copper of importance in the construction of electrical apparatus?
272. Mention the reactions which take place in the process of lead smelting.
273. What class of waters are dangerous to store in lead cisterns?
274. How would you determine whether a sample of drinking water contained any lead?
275. What advantage has lead for use in the manufacture of rifle bullets?
276. Describe the manufacture of small shot.
277. Lead combines with oxygen in several proportions; give the formulæ and preparation of the principal compounds.
278. What is the difference between "white" and "red" lead? To what purposes are they put?
279. How can the presence of lead be readily detected?
280. What happens when nitric acid is warmed with metallic lead, lead carbonate and red lead?
281. What do you understand by the terms "alloy" and "amalgam"?
282. Why are the silver and gold coins alloyed with copper, and to what extent?
283. What is the source of the metal mercury? How is it obtained pure?
284. For what purposes is mercury used extensively?
285. Distinguish between the mercurous and mercuric compounds, and show how the one can be converted into the other.
286. Give the formulæ and chemical names for the following:—Corrosive sublimate, calomel, and vermilion.
287. With what metal is silver generally found? Describe Pattinson's process for its extraction?
288. Silver does not directly combine with oxygen; to what cause is the tarnishing of silver due?
289. What is "lunar caustic"? What happens when a solution of common salt is added to silver nitrate?
290. What special properties have the salts of silver that render them useful in photographic processes?
291. In the solar spectrum, what rays are most chemically active?

292. What chemical change does chloride of silver undergo when acted on by white light? Is this change always apparent to the eye?
293. What advantages has the dry process over the wet process in photography?
294. By what means is the developed image on a plate made permanent?
295. What materials are used in the ferrotype and carbon processes?
296. What methods have been successfully employed in extracting gold?
297. What action has nascent chlorine on gold, and how would you proceed to dissolve up a gold ornament?
298. What is "Purple of Cassius"? What use has it in the manufacture of certain kinds of glass?
299. Why are gold and platinum classed with the noble metals?
300. Of what use is platinum tetrachloride in analytical chemistry?
301. What substances must not be fused in platinum crucibles and why?
302. What special properties does the metal platinum possess and to what uses are these put?
303. What happens when white light falls on an opaque body, and on a transparent body?
304. Why dose a rose appear red?
305. What physical states alter the appearance of a solid substance?
306. Describe the process of manufacturing white lead? What advantages does zinc white have over white lead?
307. What chemical change takes place in the blackening of white lead?
308. Why are the black pigments so permanent?
309. What precautions must be taken when red oxide of iron is used for painting ironwork, and why is it necessary to have the substance pure?
310. What is red lead? To what special purposes is it put?
311. Give the composition of vermilion? Describe how it can be prepared from cinnabar and metallic mercury.
312. Give a short account of the organic reds? What do you understand by a "lake"?
313. What yellow pigments are most permanent, and why?
314. What advantages does cadmium yellow possess over yellow ochre?
315. Give a list of the green pigments containing copper? What other metal is generally associated with copper?
316. What happens when a mixture of Prussian blue and burnt sienna is exposed to sunlight in moist air?
317. How is Prussian blue obtained as a precipitate, and in solution?
318. What is the source of indigo, and how is it used in processes of dyeing?
319. What acid is used to dissolve indigo?
320. Give the names of the brown pigments?
321. What natural causes combine to destroy the colour of most pigments?
322. Under what condition is a water colour painting most permanent?
323. What particular rays in white light are the most active in producing fading?

APPENDIX.

AVOIRDUPOIS WEIGHT.

1 lb. = 16 oz. = 7,000 grains.
1 oz. = 437.5 grains.

1 gallon weighs 10 lb. av., or 70,000 grains.
1 pint contains 20 fluid oz.
1 cubic ft. of water weighs 997 oz. = 1,000 oz. nearly.

APOTHECARIES' WEIGHT.

1 lb. = 12 oz. = 5,760 grains.
1 oz. = 480 grains.

MEASURES OF LENGTH.

Meter = 39·37 inches.
Decimeter = $\frac{1}{10}$ meter = 3·937 ,,
Centimeter = $\frac{1}{100}$,, = ·3937 ,,
Millimeter = $\frac{1}{1000}$,, = ·03937 ,,

MEASURES OF CAPACITY.

Liter = 1,000 cubic centimeters = 61.024 cubic inches = 1.76 imperial pint.
Cubic centimeter = $\frac{1}{1000}$ liter.

MEASURES OF WEIGHT.

Kilogram = 1,000 grams = 15432 grains = 2.2 lbs. av.
Gram = $\frac{1}{1000}$ kilogram = 15.432 grains.
Decigram = $\frac{1}{10}$ gram.
Centigram = $\frac{1}{100}$,,
Milligram = $\frac{1}{1000}$,,
1 cubic meter of water weighs 0.9842 ton.

Table of the corresponding Heights of the Barometer in Millimeters and English Inches.

Milli-meters.	=	English inches.	Milli-meters.	=	English inches.	Milli-meters.	=	English inches.
720	=	28.347	739	=	29.095	758	=	29.843
721	=	28.386	740	=	29.134	759	=	29.882
722	=	28.425	741	=	29.174	760	=	29.922
723	=	28.465	742	=	29.213	761	=	29.961
724	=	28.504	743	=	29.252	762	=	30.000
725	=	28.543	744	=	29.292	763	=	30.039
726	=	28.583	745	=	29.331	764	=	30.079
727	=	28.622	746	=	29.370	765	=	30.118
728	=	28.662	747	=	29.410	766	=	30.158
729	=	28.701	748	=	29.449	767	=	30.197
730	=	28.740	749	=	29.488	768	=	30.236
731	=	28.780	750	=	29.528	769	=	30.276
732	=	28.819	751	=	29.567	770	=	30.315
733	=	28.858	752	=	29.606	771	=	30.355
734	=	28.898	753	=	29.645	772	=	30.394
735	=	28.937	754	=	29.685	773	=	30.433
736	=	28.976	755	=	29.724	774	=	30.473
737	=	29.016	756	=	29.764	775	=	30.512
738	=	29.055	757	=	29.803			

For Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
—90°	—130°	—60°	—76°	—30°	—22°
85	121	55	67	25	13
80	112	50	58	20	4
75	103	45	49	15	+ 5
70	94	40	40	10	14
65	85	35	31	5	23

For Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale—(continued).

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
0°	+32°	+100°	+212°	+200°	+392°
+ 5	41	105	221	205	401
10	50	110	230	210	410
15	59	115	239	215	419
20	68	120	248	220	428
25	77	125	257	225	437
30	86	130	266	230	446
35	95	135	275	235	455
40	104	140	284	240	464
45	113	145	293	245	473
50	122	150	302	250	482
55	131	155	311	255	491
60	140	160	320	260	500
65	149	165	329	265	509
70	158	170	338	270	518
75	167	175	347	275	527
80	176	180	356	280	536
85	185	185	365	285	545
90	194	190	374	290	554
95	203	195	383	295	563

1° C. = 1.8° F.
2 = 3.6
3 = 5.4
4 = 7.2

Table of the Tension of Aqueous Vapour expressed in Inches of Mercury, at 32° F., for each degree F. between 0° and 100°.

Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.
0	0.0439	26	0.1395	51	0.3742	76	0.8964
1	0.0459	27	0.1457	52	0.3882	77	0.9266
2	0.0481	28	0.1522	53	0.4026	78	0.9577
3	0.0503	29	0.1589	54	0.4175	79	0.9898
4	0.0526	30	0.1660	55	0.4329	80	1.0227
5	0.0551	31	0.1733	56	0.4488	81	1.0566
6	0.0576	32	0.1810	57	0.4653	82	1.0915
7	0.0603	33	0.1883	58	0.4822	83	1.1274
8	0.0630	34	0.1959	59	0.4997	84	1.1643
9	0.0659	35	0.2038	60	0.5178	85	1.2023
10	0.0689	36	0.2119	61	0.5364	86	1.2413
11	0.0721	37	0.2204	62	0.5556	87	1.2815
12	0.0753	38	0.2291	63	0.5755	88	1.3228
13	0.0788	39	0.2381	64	0.5959	89	1.3652
14	0.0823	40	0.2475	65	0.6170	90	1.4088
15	0.0861	41	0.2571	66	0.6388	91	1.4537
16	0.0899	42	0.2672	67	0.6612	92	1.4998
17	0.0940	43	0.2775	68	0.6843	93	1.5471
18	0.0982	44	0.2882	69	0.7081	94	1.5958
19	0.1027	45	0.2993	70	0.7327	95	1.6457
20	0.1073	46	0.3108	71	0.7580	96	1.6971
21	0.1121	47	0.3226	72	0.7841	97	1.7498
22	0.1171	48	0.3349	73	0.8109	98	1.8039
23	0.1223	49	0.3476	74	0.8386	99	1.8595
24	0.1278	50	0.3607	75	0.8671	100	1.9170
25	0.1335						

Boiling Point and Latent Heat of Water under varying Pressures.

Pressure.	Boiling point.	Latent heat.
1 atmosphere	212° Fahr.	966 thermal units.
2 ,,	249° ,,	940 ,,
3 ,,	273° ,,	923 ,,
4 ,,	291° ,,	910 ,,
5 ,,	306° ,,	900 ,,
6 ,,	319° ,,	891 ,,

Specific Heats of more common Elements.

Elements.	Specific heat $=w$.	Atomic weight $= a$	Atomic Heat $w \times a$
Hydrogen	5.880	1	5.9
Boron	0.254	10.9	2.8
Carbon (as diamond)	0.174	12	2.1
Sodium	0.293	23	6.7
Magnesium	0.245	23.9	5.9
Aluminium	0.202	27.3	5.5
Silicon (cryst.)	0.165	28	4.6
Phosphorus (yellow)	0.189	31	5.9
Sulphur (rhombic)	0.178	32	5.7
Potassium	0.166	39	6.5
Calcium	0.170	39.9	6.8
Chromium	0.100	52.4	5.2
Manganese	0.122	54.8	6.7
Iron	0.112	55.9	6.3
Cobalt	0.107	58.6	6.3
Nickel	0.108	58.6	6.4
Copper	0.093	63.2	5.9
Zinc	0.093	64.9	6.1
Arsenic (cryst.)	0.082	74.9	6.2
Selenium (cryst.)	0.080	78.9	6.4
Bromine (solid)	0.084	79.7	6.7
Molybdenum	0.072	95.8	6.9
Palladium	0.059	106.2	6.3
Silver	0.056	107.6	6.0
Cadmium	0.054	111.9	6.0
Tin	0.054	117.5	6.5
Antimony	0.052	119.6	6.2
Tellurium	0.047	125	6.0
Iodine	0.054	126.5	6.8
Platinum	0.032	194.5	6.3
Gold	0.032	196 2	6.4
Mercury (solid)	0,032	200	6.4
Lead	0.031	206.4	6.5
Bismuth	0.030	207	6 5
Uranium	0.027	240	6.6

Substances employed in so-called Freezing Mixtures.	Approximate lowest Temperature obtained.
Water and ammonic nitrate (1 : 1)	—16° C
Crystallised sodic sulphate and hydrochloric acid (8 : 5)	—18°
Snow and common salt (1 : 1)	—18°
Snow and calcic chloride (1 : 1)	—45°
Ether and solid carbon dioxide	—77°
Carbon bisulphide and liquid nitrous oxide	—140°

Density of Sea Water on various Scales.

Density or specific gravity 1.025 at 0° C = $\frac{1}{32}$ salinometer = 10° densimeter.
,, ,, 1.05 ,, = $\frac{2}{32}$,, = 20° ,,
,, ,, 1.09 ,, = $\frac{3}{32}$,, = 30° ,,
,, ,, 1.2 ,, = $\frac{7}{32}$,, = 70° ,,

THE PERIODIC LAW.

Amongst the various attempts made to classify the elements, the most complete and comprehensive is that proposed by J. A. R. Newlands, under the name of the "Law of Octaves." Newlands showed that if the elements are arranged in the order of their atomic weights, there is a regular reappearance of similar properties in every eighth element. This periodicity is of great importance in checking the accepted atomic weights of certain elements, and also in enabling the chemist to predict the existence and even the properties of unknown elements. Mendelejeff, who has most completely worked out this law, and calls it the "Periodic Law," arranges the elements in eight groups and twelve series, as shown in the table on *page* 485.

In this table it will be seen that the members of each group show similarity in their chemical and physical characters, more especially of the even and odd series respectively. On the other hand, the members of one series show a gradual gradation of properties, as we proceed from one member to the other. The places where a query is placed in the table, indicate the probable existence of unknown elements.

Series.	GROUP. I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H = 1							
2	*Li = 7*	*Be = 9*	*B* = 11	*C = 12*	*N = 14*	*O = 16*	*F = 19*	
3	Na = 23	Mg = 24	Al = 27·1	Si = 28	P = 31	S = 32	Cl = 35·5	
4	*K = 39*	*Ca = 40*	*Sc = 44*	*Ti = 48*	*V = 51·3*	*Cr = 52*	*Mn = 55*	*Fe = 56 Co = 58.6 Ni = 58.6*
5	Cu = 63·2	Zn = 65	Ga = 70	?	As = 75	Se = 79	Br = 80	
6	*Rb = 85*	*Sr = 87*	*Y = 89* ?	*Zr = 90*	*Nb = 94*	*Mo = 95·5*	*100*	*Ru = 104 Rh = 104*
7	Ag = 107·7	Cd = 112	In = 113·4	Sn = 117·5	Sb = 120	Te = 125	I = 126·5	
8	*Cs = 133*	*Ba = 137*	*La = 138*	*Ce = 140*	*Di = 142*	*Tb ? = 148·8*	*Sm? = 150*	*? 152 ? ?*
9	?	?	Dp ? 159	?	Er ? 165·9	?	?	
10	*?*	*?*	*Yb = 173*	*?*	*Ta = 182*	*W = 184*	*?*	*Os 195 ? Ir = 192·5 Pt = 194.5*
11	Au = 196	Hg = 200	Tl = 204	Pb = 206	Bi = 207·5	Ng ? 214	?	
12	*?*	*?*	*?*	*Th = 232*	*?*	*U = 239*	*?*	

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